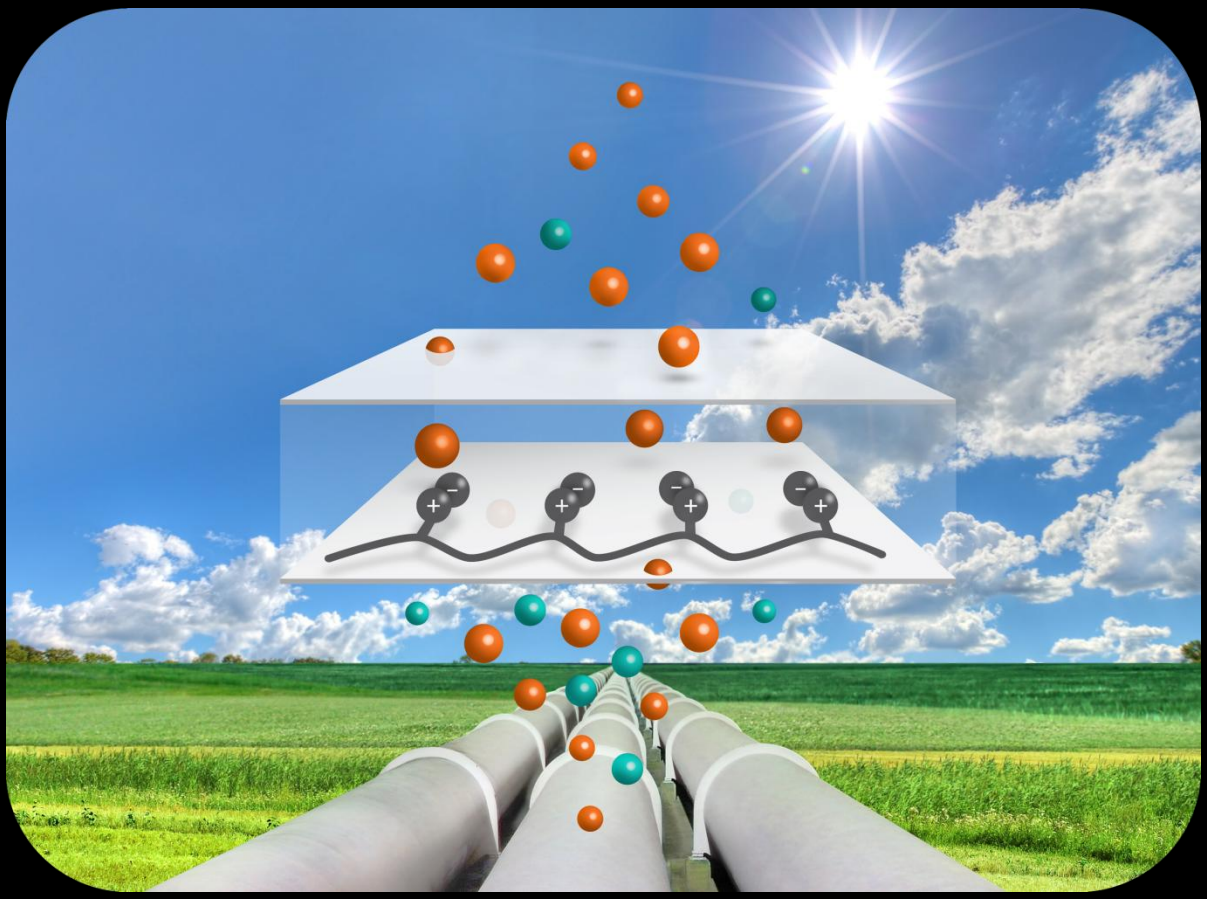
Development of new membranes based on ionic liquid materials for gas separation

Liliana C. Tomé



Dissertation presented to obtain the Ph.D degree in
Engineering and Technology Sciences, Chemical Engineering

Instituto de Tecnologia Química e Biológica António Xavier | Universidade Nova de Lisboa

Oeiras
December, 2014

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Knowledge Creation

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Second Edition, January 2015

I declare that the work presented in this thesis, except where otherwise stated, is based on my own research. The work was mainly performed in the Molecular Thermodynamics Laboratory of the Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa, between June 2011 and December 2014, and supervised by Doctor Isabel Marrucho (ITQB-UNL) and Doctor Carmen Freire (CICECO-UA). Part of the results was attained during visiting periods to Macromolecular and Lignocellulosic Group, CICECO, Department of Chemistry, University of Aveiro, and to the Institute for Polymer Materials (POLYMAT), University of the Basque Country, Donostia-San Sebastian, Spain.

Financial support was provided by Fundação para a Ciência e a Tecnologia through the doctoral fellowship SFRH/BD/72830/2010.

Ao meu Pai…

"Entre sorrisos, lágrimas ou saudades.
Feliz ou com o coração apertado.
Continuo, sempre que preciso,
a juntar a minha à tua voz.
A força não sou só eu,
a força somos nós"

Acknowledgments

"O valor das coisas não está no tempo que elas duram, mas na intensidade com que acontecem. Por isso, existem momentos inesquecíveis, coisas inexplicáceis e pesssoas incomparáveis"

Fernando Pessoa

Às minhas orientadoras, Doutora Isabel Marrucho e Doutora Carmen Freire, pela orientação científica e conhecimentos transmitidos, pelo apoio e compreensão, mas principalmente por terem acreditado sempre em mim e no meu trabalho mesmo quando eu ainda não acreditava!

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A todos os meus colegas do ITQB que de alguma forma me acompanharam e fizeram sentir bem no dia a dia, mas principalmente àqueles que se tornaram amigos para a vida. Ao Filipe *"suppaslice"* com o seu coração de ouro, mais que um amigo, um verdadeiro *"brother in arms"*, obrigada por teres estado sempre presente! Ao gang, das noitadas a trabalhar no lab, dos jantares de frango assado do Continente e dos conselhos científicos altamente secretos (Helga, Rui, Filipe e David), obrigada por todo o vosso apoio, força e amizade incondicional. À Filipa que partiu cedo em busca da sua aventura, mas que deixou a sua marca e muitas saudades. À Catarina e à Andreia, as duas carcaças preferidas, obrigada por todas as nossas pausas para café, pelas parvoíces e descontração, mas sobretudo pelo incentivo e preocupação! Bem… acho que nunca tantas asneiras foram ditas dentro do ITQB como quando a malta que está, já passou, ou vai passando pelo lab do 7º se junta, mas para mim foi excelente!

Agradeço também todas as oportunidades que tive de viajar, conhecer outras pessoas e lugares, de viver momentos que muito contribuíram para o meu crescimento a nível profissional e pessoal…

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Um agradecimento muito especial à minha família - mãe, mana, mano, cunhado, sobrinha - pelo apoio contínuo, por compreenderem as longas ausências e faltas de dedicação, por me terem ajudado a crescer e a viver da melhor forma, por terem sempre confiado e acreditado em mim mesmo naqueles momentos que sentimos que a Força nos tinha abandonado… sem vocês nunca teria conseguido!

A todos os "*incomparáveis"* que me acompanharam
neste *"inesquecível"* caminho…
Muito Obrigado!

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Contents

Development of new membranes based on ionic liquid materials for gas separation

Abstract

In the field of energy, natural gas is an essential bridge to a clean, low carbon, renewable energy era. However, natural gas processing and transportation regulation require the removal of contaminant compounds such as carbon dioxide (CO_2). Regarding clean air, the increasing atmospheric concentrations of greenhouse gases, specifically CO_2, is of particular concern. Therefore, new cost-effective, high performance technologies for carbon capture have been researched and the design of materials with the ability to efficiently separate CO_2 from other gases is of vital importance.

Taking into account the extremely broad range of chemical and structural possibilities of ionic liquid (IL) chemistry, and the undeniable engineering and economical advantages of membrane technology, this thesis explores the use of IL-based materials to prepare membranes not only for the selective separation of CO_2 from CH_4 and N_2 (Chapter 2 to 7), but also for olefin/paraffin separation (Chapter 8). The data presented throughout these chapters clearly show that the endless combination of cations and anions or the incorporation of specific chemical groups allow the development of new membranes for more efficient and sustainable gas separation processes.

This thesis presents a perspective of different straightforward strategies for designing new efficient gas separation membranes based on ILs (Chapter 2 and 3) and their polymers (PILs) and composites (PIL–IL) (Chapter 4 to 8). The idea is not only to show the versatility of these ionic materials in the development of improved gas separation membranes but also their easy preparation. The obtained results are innovative and capable of unraveling specific structure-relationship properties of membrane materials with new functionalities never explored. Due to the promising data obtained, it is foreseen that the prepared engineered membranes will play a especial role as alternative efficient materials, in particular for flue gas separation, natural gas purification, and light olefin/paraffin separation.

Resumo

No campo da energia, o gás natural apresenta-se como uma ponte essencial para uma nova era de energias limpas, renováveis e com baixo teor em carbono. No entanto, processamento e transporte do gás natural requerem a remoção de contaminantes, como por exemplo o CO_2. No que diz respeito ao ar puro, a aumento da concentração de gases de estufa, especificamente CO_2, na atmosfera encorajaram a investigação de novas tecnologias de captura de CO_2, eficientes e simultaneamente baratas, assim como o desenvolvimento de materiais com a capacidade de separar eficientemente o CO_2 de outros gases.

Tendo em conta as propriedades únicas dos liquidos iónicos e uma vez que as tecnologias de separação baseadas em membranas apresentam vantagens inegáveis, quer do ponto de vista da engenharia, quer do ponto de vista económico, esta tese explora a utilização de materiais à base de liquidos iónicos para preparar membranas não só para a separação selectiva de CO_2 (Capítulo 2 a 7), mas também para separação de olefinas/parafinas (Capítulo 8). Os dados apresentados ao longo destes capítulos mostram claramente que a combinação apropriada de catiões e aniões ou a incorporação de grupos químicos específicos permitem o desenvolvimento de novos processos para membranas de separação de gás mais eficientes e sustentáveis.

Esta tese apresenta uma perspectiva de diferentes estratégias simples para a preparação de novas membranas mais eficientes para a separação de gases, com base em liquidos iónicos (Capítulo 2 e 3) e seus polímeros (PILs) e compósitos (PIL–IL) (Capítulo 4-8). A ideia é, não só mostrar a versatilidade destes materiais iónicos no desenvolvimento de melhores membranas de separação de gases, mas também revelar a sua fácil preparação. Os resultados obtidos são inovadores e capazes de desvendar a relação entre algumas propriedades e a estrutura específica das membranas preparadas com novas funcionalidades que nunca foram exploradas. Devido aos resultados promissores que foram obtidos, prevê-se que as membranas preparadas podem vir a ter um papel especial como materiais alternativos mais eficientes, em particular, para a separação dos gases de combustão, purificação de gás natural, e separação de olefinas/parafinas.

Publications

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L.C. Tomé, M. Isik, C.S.R. Freire, D. Mecerreyes, I.M. Marrucho, Novel pyrrolidinium-based polymeric ionic liquids with cyano counter-anions: high performance membrane materials for post-combustion CO_2 separation, *submitted manuscript,* 2015.

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L.C. Tomé, M.G. Freire, L.P.N. Rebelo, A.J.D. Silvestre, C.P. Neto, I.M. Marrucho, C.S.R. Freire, Surface hydrophobization of bacterial and vegetable cellulose fibers using ionic liquids as solvent media and catalysts. *Green Chem.* (2011), **13**, 2464-2470.

L.C. Tomé, R.J.B. Pinto, E. Trovatti, C.S.R. Freire, A.J.D. Silvestre, C.P. Neto, A. Gandini, Transparent bionacomposites with improved properties prepared from acetylated bacterial cellulose and poly(lactic acid) through a simple approach. *Green Chem.* (2011), **13**, 419 - 427.

C.M.B. Gonçalves, **L.C. Tomé**, J.A.P. Coutinho, I.M. Marrucho, Addition of α-Tocopherol on Poly(lactic acid): Thermal, Mechanical and Sorption Properties. *J. Appl. Polym. Sci.* (2011), **119**, 2468-2475.

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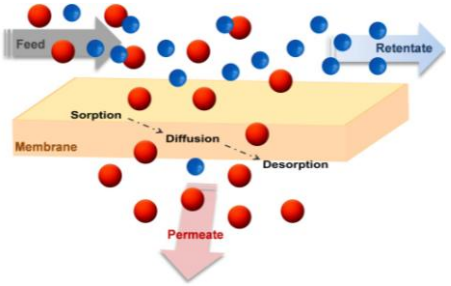
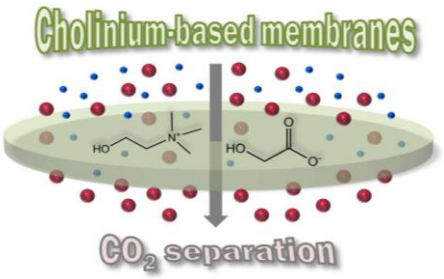
Thesis Layout

Chapter 1 – Introduction



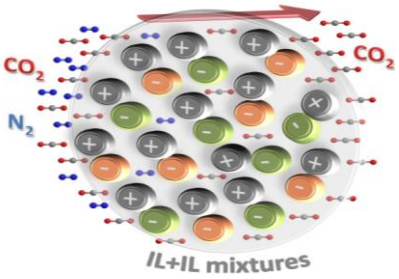
An overview of the background and general concepts which fall within the scope of this thesis will be presented.

Chapter 2 – Cholinium-based supported ionic liquid membranes: a sustainable route for CO_2 separation



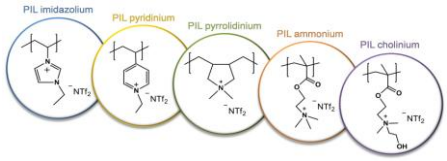
Aiming at full sustainability of CO_2 separation processes, membranes based on environmental-friendly cholinium carboxylate ionic liquids were successfully prepared.

Chapter 3 – Playing with ionic liquid mixtures to design engineered membranes for CO_2 separation



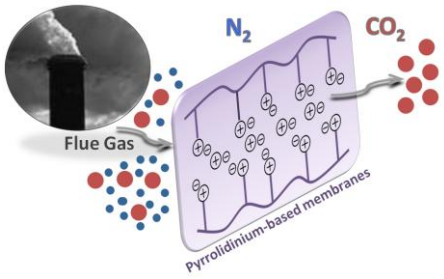
In order to increase the flexibility in tailoring the permeability and selectivity of supported ionic liquid membranes for CO_2 separation, the use of ionic liquid mixtures is explored.

Chapter 4 – Polymeric ionic liquid membranes: influence of polycation variation



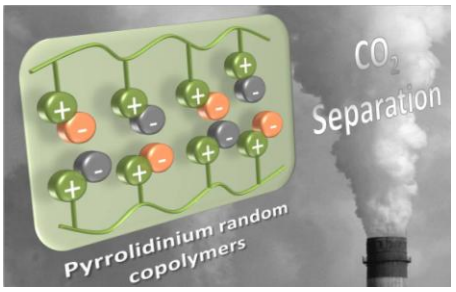
With the intent of fully explore the influence of polycation functionality, membranes based on cationic PILs containing in their backbones the most important ionic liquid cations were prepared and their gas permeation properties presented.

Chapter 5 – Pyrrolidinium-based polymeric ionic liquid materials for CO_2 separation



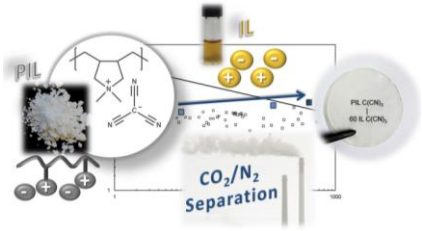
The feasibility of using pyrrolidinium-based materials to prepare CO_2 separation membranes is addressed. Membranes within the whole range of compositions, from pure polymer to pure ionic liquid, encompassing PIL–IL composites, were evaluated.

Chapter 6 – Polymeric ionic liquids with mixtures of counter-anions for CO_2 separation



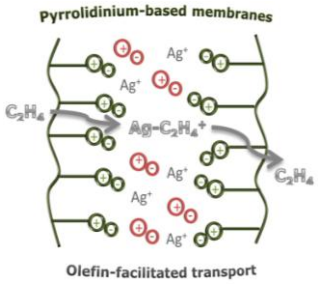
A new family of pyrrolidinium random copolymers containing different anion mixtures was synthesized by simple salt metathesis reactions and PIL–IL composite membranes were successfully prepared. Their mechanical and gas permeation properties are provided.

Chapter 7 – Pyrrolidinium-based polymeric ionic liquids with cyano counter-anions for CO_2 separation



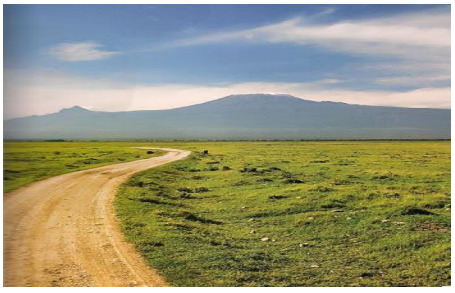
The synthesis of novel pyrrolidinium-based PILs containing different cyano-functionalized anions is described. The potential of the prepared composite membranes for highly efficient post-combustion CO_2 separation is shown.

Chapter 8 – Polymeric ionic liquid membranes containing IL–Ag^+ for ethylene/ethane separation



The use of PILs as alternative polymer matrices to prepare membranes for ethylene/ethane separation is addressed. PIL–IL–Ag^+ membranes were successfully prepared and their ethane and ethylene permeation properties discussed.

Chapter 9 – Concluding Remarks & Outlook



The main achievements and conclusions are highlighted herein. Possible challenges and perspectives for future research are also presented.

Thesis Guidelines

This thesis is divided into nine chapters. Chapter 1 introduces the context and motivation, general concepts on CO_2 separation technologies, as well as a revision of the state of the art focusing on the use of ionic liquid-based materials for CO_2 separation. Although this chapter contains essential information for understanding the subsequent chapters enclosed in this thesis, it does not aim at providing a comprehensive revision of all the subjects herein presented.

The subsequent chapters are entirely based on scientific articles and focus on designing membranes for CO_2 separation via two different straightforward approaches: the first makes use of supported ionic liquid membranes (Chapter 2 and 3) for the selective separation of CO_2 from CH_4 and N_2, while the second takes advantage of solid composite membranes not only for CO_2 separation (Chapter 4 to 7) but also for olefin/paraffin separation (solely and completely described in Chapter 8).

Bearing in mind that this is an article-based thesis, each chapter includes a review of the pertinent the state of the art, describes the materials and methods used, presents and discusses the results and draws the main conclusions of that particular work. Also, this thesis does not contain general list of figures and/or symbols since figure captions, symbols and abbreviations are carefully identified and described in each chapter.

In fact, Chapters 2 to 8 are individual article-based chapters, which were not put together by their chronological order of publication, but rather to give the reader a flavor of the authors vision on this emerging field. No effort was made to bind the chapters together, by referring either previous or subsequent chapters. However, this specific sequence of chapters provides a view from the simpler implementation of ionic liquids as gas separation membranes to a more complex approach where polymeric ionic liquids were prepared and tested. The thesis as a

whole also provides interesting analogies between ionic liquids and polymeric ionic liquids, considering that the first can be used as a tool for the estimation of the permeation properties of specific anions or functional groups. Since this thesis presents the first evaluation for the membranes prepared during this PhD work, only gas permeation experiments using pure gases were performed.

Ultimately, in Chapter 9, the main conclusions are withdrawn and discussed in an integrated way. Some perspectives for future research are also presented.

Chapter 1

Introduction

Sections 5 and 6 contain parts of the following author's publication: **L.C. Tomé** and I.M. Marrucho, Poly(ionic liquid)s: Designing CO_2 separation membranes, in Applications of Ionic Liquids in Polymer Science and Technology, *Springer*, in press, 2015.

This chapter describes in detail the context and motivation of the present thesis, the background and general concepts, and the progressive development of the state of the art of ionic liquid (IL)-based materials as new alternatives for CO_2 separation membranes, in particular for flue gas separation (CO_2/N_2) and natural gas purification (CO_2/CH_4). Finally, the objectives and the structure of the present thesis are presented.

1. The context

Climate change and renewable energy are two of the most important societal challenges that our world faces today.[1] The search for new environmentally acceptable solutions is being urged by governments through the implementation of stricter legislation and the development of new collaborative research programs.

In the field of energy, natural gas stands today as an essential bridge to a clean, low carbon, renewable energy era. In order to maintain and expand the availability of this clean burning and efficient fuel source, natural gas processing regulations require the removal of contaminants such as H_2S and CO_2 since they not only reduce the heating value of the methane gas streams in power plants, but also cause corrosion in pipes and equipment.[2] On the other hand, the increasing atmospheric concentrations of greenhouse gases, specifically CO_2, is of particular concern due to the resulting significant environmental risks which are largely associated to unpredictable climate changes. From 1975 to 2013 the CO_2 concentration in the atmosphere has monotonically increased from 277 to 395 ppm.[3] Actually, billions of tons of annual CO_2 emissions are a direct sub-product of fossil fuel combustion (i.e. petroleum, coal, and natural gas) for generation of energy and heat.[4]

There are a number of means to reduce the CO_2 emissions to the atmosphere, including higher efficiency processes for energy production,

replacing current fossil fuel-based energies by more environmentally benign sources (renewable energy), and Carbon Capture and Storage (CCS). Despite the extensive research efforts on the use of energy from renewable sources, currently fossil fuels are the major source of energy and are predicted to remain in this position for at least the next couple of decades. Thus, as the transition to more sustainable energy processes progresses, there is a great interest in the development of highly efficient technologies to curb CO_2 emissions of the current energy sources. In this context, CCS is a viable strategy that provides a short-term solution to lessen climate change until renewable energy technologies mature.[5]

CCS is a relatively new term that is usually applied to describe processes for capturing anthropogenic CO_2 from large point sources, with the prototypical target being large coal-fired power plants. Therefore, processes and materials to capture and concentrate CO_2 from these point sources are needed, followed by compression, transport and permanent storage, for example, in underground geological formations, depleted oil fields and gas formation, or in deep saline aquifers.[6] However, several technical challenges must be overcome to make CCS practical and cost effective, including the development of materials that enable the efficiently separation of CO_2, the design of appropriated CCS processes that can be integrated into existing power generation infrastructures, and safe methods for sequestering CO_2.[7] All of these key needs have prompted the chemical science and engineering communities to develop and provide novel, practical solutions to global carbon management.

Although various components of the CCS process chain are technologically mature and available,[8] the existing methods for CO_2 separation are highly energy intensive and can drastically increase the energy requirements of a plant by 25 – 40%.[9] Since the energy input for materials regeneration and the capital cost of specific equipments are the most significantly contributors to the overall cost of CO_2 capture,[10] new cost-effective and high performance technologies need to be

researched and consequently the design of materials with the ability to efficiently separate CO_2 from other gases is of vital importance.

Nowadays, many challenges are being faced in order to achieve improved processes and materials. Nonetheless, enhancing the CO_2 separation efficiency of a material has enormous potential for lowering the cost of CO_2 capture systems in a near-term and represents one of the foremost challenges.[11]

2. CO_2 capture/separation technologies

Three CO_2 separation processes hold the promise for the reduction CO_2 emissions, namely CO_2 removal in natural gas sweetening (CO_2/CH_4), CO_2 recovery from power plant flue streams (CO_2/N_2), and CO_2 separation from fuel gas (syngas) in hydrogen production (CO_2/H_2). These industrial processes emit CO_2 streams with distinct compositions and consequently the CO_2 separation from light gases (e.g. CH_4, N_2, and H_2) is a key technical, economical and environmental challenge.

In post-combustion capture from flue gas, the major obstacle is the lower pressure of the flue gas (ca. 100 kPa). Additionally, the CO_2 concentration is also low (roughly 15%) and the capture requires its separation from a high volume stream of flue gas containing other component gases, predominantly N_2.[12] Raw natural gas varies substantially in composition depending on the source (75% - 90% of CH_4) and the reserves are typically contaminated with undesirable impurities, such as CO_2. The removal of CO_2 would increase not only the energy density of natural gas making its storage and transportation more efficient, but also its conversion to hydrogen fuel.[2] An efficient CO_2 separation from other natural gas components at high pressures is required.[13] Regarding CO_2 separation from fuel gas (output from gasification and water-gas shift reactors), it occurs under high pressures (> 2000 KPa) and temperatures (> 473 K) conditions, where the relevant pre-combustion separation is CO_2/H_2.[14, 15]

The most relevant technologies currently used to separate CO_2 from a gas stream are solvent-based chemical absorption, adsorption with porous solids, cryogenic distillation and membranes.[16-20]

2.1. Solvent absorption

Solvent absorption (Figure 1) with amines is undoubtedly the most efficient technology.[21] Some of the commonly used solvents are: primary amines such as monoethanolamine (MEA), 2-amino-2-methyl-1-propanol (AMP); secondary amines such as diethanolamine (DEA); and tertiary amines such as methyldiethanolamine (MDEA).[10] Despite their advantages, such as high reactivity and good absorption capacity, the use of amines is of environmental and economical concern due to their corrosive nature, volatility and high energy demand for regeneration.[4, 17, 20]

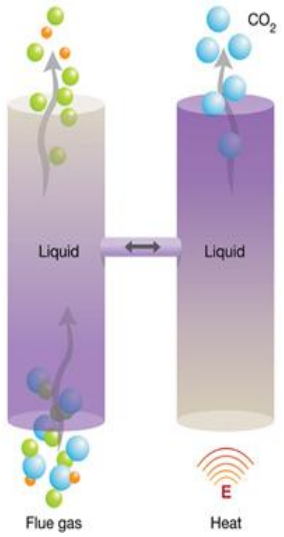


Figure 1| Schematic representation of CO_2 separation by solvent-based absorption technology.[22]

2.2. Adsorption with porous solids

Adsorption processes with porous solids (Figure 2) is an advantageous technology compared to solvent-based absorption, since it presents easy operation, rapid rate, low corrosion, and low energy demand for regeneration. There are different methods to regenerate the solid adsorbents after the CO_2 capture, namely vacuum and pressure swing adsorption (VSA and PSA), temperature swing adsorption (TSA), and electric swing adsorption (ESA).[23] Aluminosilicates, titanosilicates, molecular sieves and activated carbons are examples of typical commercial CO_2 selective adsorbents.[18] Moreover, metal organic frameworks and zeolites have been proposed and investigated as possible advanced sorbents for CO_2 separation.[24-26] Despite the progresses achieved in their preparation, additional research about how to improve their stability, to reduce their cost and other technological parameters is still need before their industrial application. The best adsorbents should have high CO_2 capacity and selectivity, fast adsorption/desorption kinetics, good mechanical properties and high thermal and chemical stability, as well as low costs of synthesis.[8, 23]

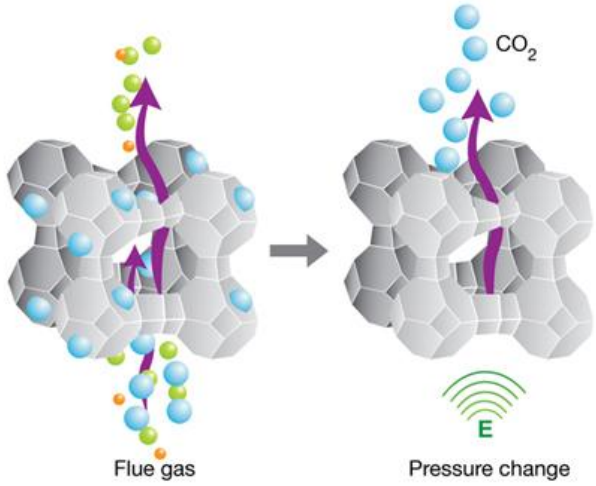


Figure 2| Schematic representation of CO_2 adsorption with porous solids.[22]

2.3. Cryogenic distillation

Cryogenic distillation is a technique that is based on cooling and condensation (Figure 3). It has been used in liquid separation for a long time. This technology is hypothetical very useful for CO_2 separation since no chemical absorbents are required to obtain high purity gases, but the high energy requirements make it less desirable for most gas separation applications.[16] Cryogenic distillation is more suitable when the gas streams contain high CO_2 concentrations and has being implemented for oxygen production in oxy-fuel combustion.[10]

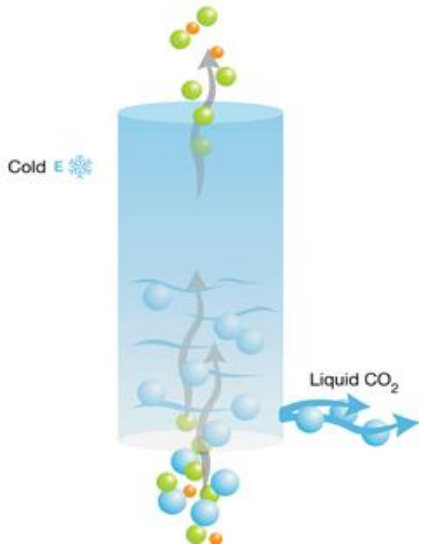


Figure 3| Schematic representation of CO_2 separation by cryogenic distillation.[22]

2.4. Membrane technology

Membranes separate gases based on the differences in physical and/or chemical interactions between the different gases and the membrane material, which allow for some components to pass preferentially through the membrane (Figure 4). This technology can be a powerful tool for CO_2 capture/separation processes due

to their engineering and economical advantages. In fact, the inherent simplicity of membranes can bring many advantages compared to other conventional separation technologies, namely the small scale of the equipment, reduced environmental impact, ease of incorporation into existing processes, low energy consumption and operating costs.[27]

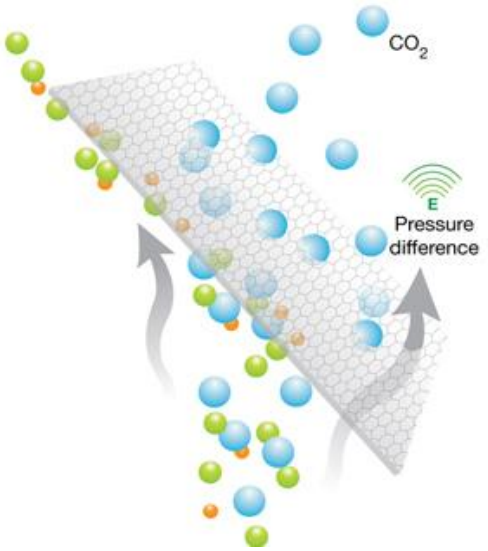


Figure 4| Schematic representation of CO_2 separation by membrane technology.[22]

In the past few decades, membrane technology has been attracting rising interest and the fast progress in the field enabled the current use of membrane-based systems on an industrial scale for different gas separations.[28] In particular, great effort is being put on the development of gas separation membrane materials for applications such as N_2 separation from air, CO_2 from natural gas, CO_2 from post-combustion flue gases, and hydrogen from various refinery and petrochemical process streams.[12, 13, 28-30] Nevertheless, to fully compete with well-established separation processes, membranes with high permeability and selectivity to specific gases, good thermal/chemical resistance and sufficient mechanical stability for withstanding the harsh environments of separation

processes, need to be developed.[28] If improved membrane materials could be obtained, this technology would grow faster and be used more widely not only in the existing applications, but also in many others new applications.[30] The search for better membranes has prompted a huge effort by many research groups and a broad range of different membrane materials have been investigated.

Depending on the material, membranes are usually classified as inorganic (ceramic, metallic, carbon molecular sieves, silica, zeolites, metal organic frameworks),[31] organic (polymeric membranes),[32] or inorganic-organic composite membranes (Mixed Matrix Membranes).[33]

Although inorganic membranes comprise important properties for CO_2 separation such as high selectivity and great thermal and chemical stability, they have high brittleness and their fabrication is very complex and requires high costs.[31, 34, 35] Alternatively, the advantages of polymeric membranes namely mechanical properties, low cost, synthetic feasibility, and large-scale production,[32] make them more attractive materials compared to inorganic membranes for gas separation.[28, 30, 32] Polymeric membranes are classified as rubbery or glassy depending on the value of their glass transition temperatures relative to working temperature. Rubbery polymers display higher gas permeability than glassy polymers, but their gas selectivities are generally lower. Glassy polymers such as cellulose acetate, polyamides, polyarylates, polycarbonates, polysulfones or polyimides have dominated the industrial CO_2 separation applications due to their good selectivities and mechanical properties.[32] Furthermore, Mixed Matrix Membranes (MMMs) is a quite recent route to enhance the properties of polymeric membranes. Their structure consists of an inorganic material, in the form of micro- or nano-fillers, incorporated into a polymeric matrix. These membranes attempt to combine the advantages of polymeric and inorganic materials, namely the desirable mechanical properties and economical processing capabilities of polymers with the high separation performance of molecular

sieving materials.[33] In principle, MMMs possess an economic advantage over inorganic membranes and they offer enhanced thermal and mechanical properties for aggressive environments, which can be a way to stabilize polymeric membranes. However, their cost and difficulties for large scale manufacture, as well as the elimination of interfacial defects between the organic matrix and the inorganic fillers have remained important challenges that need to be overcome before their commercial application.[28]

Despite the synthesis and evaluation of several hundreds of new materials, more than 90% of current commercial membranes are from fewer than ten membrane materials, most of which have been used for decades.[30] Even though polymeric membranes have achieved important success and are currently the focus of commercialization because of their easier manufacture, large improvements in CO_2 separation efficiencies require novel materials with enhanced performances. Thus, research targeted at developing new materials has been undertaken and currently the goal is to design attractive membrane structures that exhibit both higher CO_2 selectivity and permeability.[28, 30, 32]

Bearing in mind all the above mentioned aspects, and considering that ILs are a unique tunable platform for designing alternative materials, the focus of the present thesis is to explore the potential of this class of ionic materials to fabricate highly effective membranes for energy-efficient CO_2 separation.

3. Gas transport through dense membranes

The principal property of membranes used in gas separation applications is their ability to control the permeation of different species. In gas separation processes through nonporous or dense membranes, the feed gas mixture is driven by a difference in concentration or pressure across the membrane, which works as a semi-permeable barrier that restricts the movement of some gas molecules while letting other pass through, as it is depicted in Figure 5. The equations and

terminology presented below illustrate the general principles and basic concepts used to describe gas transport, as well as to evaluate the membrane material performance.

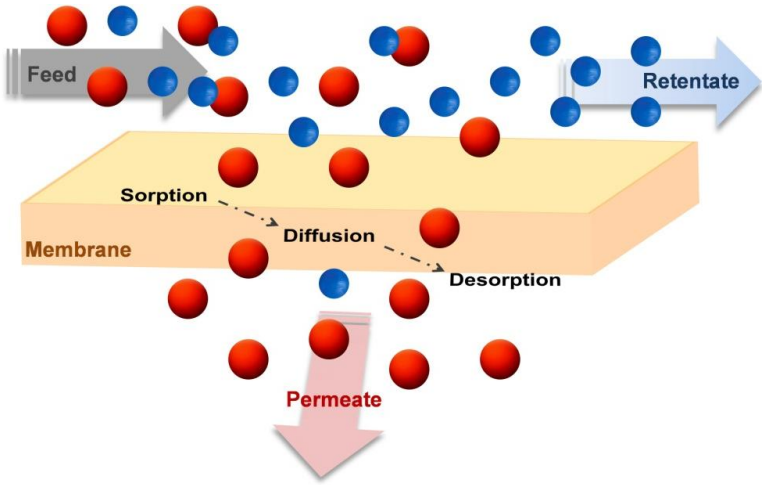


Figure 5| Schematic representation of the gas transport mechanism through dense membranes.

3.1. Permeability, diffusivity and solubility

It is generally accepted that gas transport through a dense polymeric film or liquid membrane occurs according to the solution-diffusion mass transfer mechanism, where the permeability coefficient or permeability (*P*), a measure of the membrane's ability to permeate gas, is the product of the diffusion coefficient or diffusivity (*D*) and the solubility coefficient or solubility (*S*) as follows:[36]

$$P = S \times D \quad (1)$$

Two basic assumptions underlie the solution-diffusion mechanism. The first is that gases on either side of the membrane are in equilibrium with the membrane material at the interface. The second is that the concentration and pressure differences across the membranes are dependent only on the concentration

gradient of dissolved permeant species within the membrane.[36] As it is schematically represented in Figure 5, the solution-diffusion mechanism is described by three steps: (1) gas sorption on the upstream side of the membrane, (2) diffusion of the absorbed species through the membrane driven by the concentration gradient (partial pressure difference), and (3) gas desorption on the downstream side of the membrane.[27] Consequently, permeability depends on both thermodynamic factors such as condensability of the gas specie and its interaction with membrane, and kinetic factors that are mainly governed by the size of the permeant specie, membrane material segmental mobility and packaging, fractional free volume or other structural features that permit permeant diffusion.[32]

Permeability (*P*) is defined as the steady-state gas flux (*J*) through a membrane under a transmembrane pressure drop ($\Delta p = p_2 - p_1$) and normalized to the unit thickness of the membrane:[37]

$$P = J \frac{\ell}{\Delta p} \tag{2}$$

where p_2 is the upstream pressure, p_1 is the downstream pressure and ℓ is the membrane thickness. Gas permeability is often expressed in Barrer:

$$1\,Barrer = \frac{10^{-10}\ cm^3\ (STP)\ cm}{cm^2\ s\ cmHg} \tag{3}$$

Diffusivity is an indication of the gas mobility through the membrane material and is usually expressed in $cm^2\ s^{-1}$.

Solubility (cm^3 (STP) cm^{-3} $cmHg^{-1}$), is a thermodynamic parameter which reflects the concentration of gas molecules dissolved in the membrane when equilibrated at a given gas pressure and temperature, as shown in Equation (4).[38] While solubility depends mainly on gas molecule condensability (as characterized, for example, by gas critical temperature, normal boiling point, enthalpy of

vaporization, etc.), the gas-material interactions and membrane morphological features, such as crystallinity, can also influence gas solubility.[37]

$$S = \frac{C}{p} \tag{4}$$

3.2. Selectivity

Another import parameter of a membrane is its ability to separate two gases. Membranes have different permeabilities for different gases, and the faster permeation of some gases relative to others provides the selectivity basis for using dense membranes in gas separation. The ideal permeability selectivity (or ideal separation factor), also commonly called permselectivity, $\alpha_{i/j}$,, is a measure of how well a membrane discerns one gas from another and can be determined dividing the permeability of the more permeable specie *i* by the permeability of the less permeable specie *j*.[39] Permselectivity can also be expressed as the product of the diffusivity selectivity and the solubility selectivity as follows:

$$\alpha_{i/j} = \frac{P_i}{P_j} = \left(\frac{D_i}{D_j}\right) \times \left(\frac{S_i}{S_j}\right) \tag{5}$$

Likewise permeability, the permselectivity is a material property of the membrane that is independent of its thickness.

3.3. Separation performance

The materials used to make the membrane are crucial to a specific gas separation performance. Membranes for gas separation preferably have both high permeability for a specific component of the gas mixture and high permselectivity. Higher permeability decreases the membrane area needed to treat a given amount of gas, hence decreasing the capital cost of the process, while higher permselectivity leads to gas products with higher purity. Nevertheless, a tradeoff

relationship exists between these two parameters, as polymer membranes that are more permeable are generally less selective and vice versa.[40-42] In 1991, Robeson graphically quantified this concept and showed that such tradeoff relationship can be described by the existence of an upper bound in the log-log plot of permselectivity versus permeability of the more permeable gas.[43] Due to the large amount of data available since 1991, revised upper bounds for several gas pairs were published in 2008.[44] Robeson described the correlation as:

$$P_A = k\alpha_{A/B}^{n} \quad (6)$$

where P_A is the permeability of the fast gas, $\alpha_{A/B}$ is the permselectivity, and *n* is the slope of the upper bound of the noted relationship. Bellow this line, virtually all the data points exist.[44] The upper bound relationship is an empirical correlation based on large amounts of experimental results, but a theoretical analysis performed by Freeman[39] yielded good agreement with the observed empirical results. In fact, a new concept called "upper bound" has emerged in the literature and currently this type of plot, also known as "Robeson plot", are widely used to evaluate the performance of membranes given a particular gas separation, illustrating the progress in membrane science for gas separation applications.

4. Ionic Liquids (ILs)

The first publication describing an IL is over 100 years ago, in 1914 by Paul Walden, who observed the special physical properties of ethylammonium nitrate.[45] Albeit this discovery of a new class of materials did not draw much interest at the time, ILs have gained a substantial growth and renewed interest over the last 20 years, particularly from 1995 onwards. Accordingly to the commonly accepted definition, ILs are salts entirely composed of ions (organic cations and either organic or inorganic anions), which have melting points below the conventional temperature of 100 $^{\circ}$C.[46] This general definition has been used in

order to differentiate ILs from traditional salts which melt at much higher temperatures (*e.g.* sodium chloride melts at 801 °C). The considerable lower melting temperatures of ILs outcome not only from the low intermolecular interactions and poor packing efficiency of their asymmetrical ions but also from the delocalization of their charges.

Apart from their broad definition as compounds, ILs comprise an exceptional combination of intrinsic properties such as negligible volatility,[47] thermal stability,[48] low flammability (with some rare exceptions),[49] and high ion conductivity.[50] However, their most important feature of is perhaps their tunability. This fact makes them absolutely unique and incomparable to other organic solvents, and currently most of their success stems from this property. The family of ILs is very broad since are many known and potential new cations and anions. Theoretical, there are millions of possible cation and anion combinations, though only *ca.* 300 ILs are commercially available.[46] The most commonly found cations and anions are presented in Figure 6.

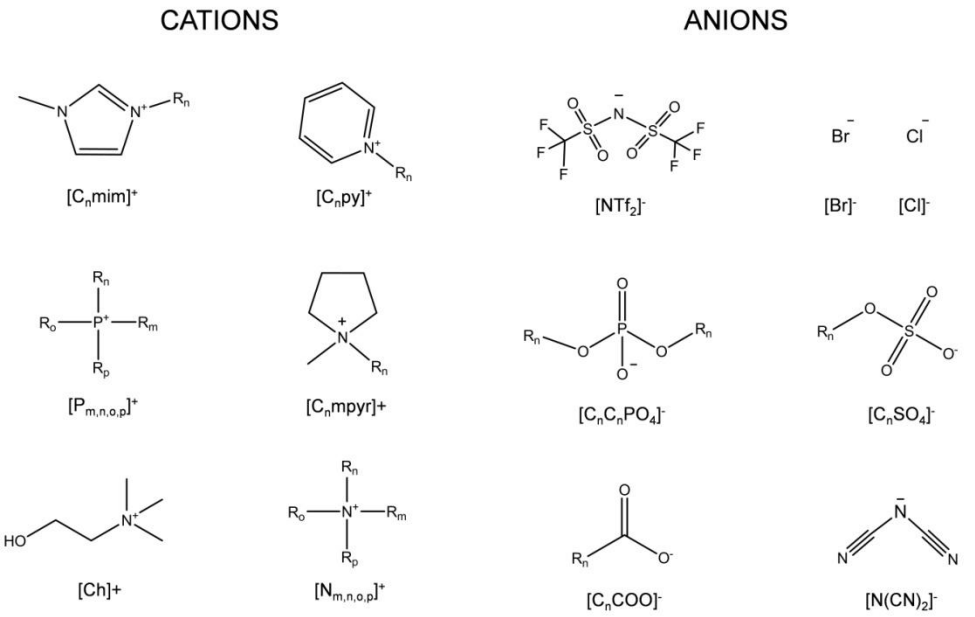


Figure 6| Cations and anions commonly used in ionic liquids.

While ILs have been advantageously used in chemical synthesis and catalysis,[51, 52] their use as novel functional materials for a huge number of different applications,[53-60] including for gas separation processes,[61-65] has also been playing a vital role in their wide disseminations. So far, in the context of gas separation, CO_2 capture/separation has been the most successful and widely studied application due to the fact that the quadrupole moment of the CO_2 molecules interacts with the electrical charges of the ILs. It is important to emphasize here that the most important features of ILs within the CO_2 separation context are not only their remarkable CO_2 solubility and selectivity over other light gases, but also the ability to tailor many of their physical and chemical properties as well as their CO_2 affinity by combining different cations and anions or by adding functional groups.

Despite the fact that ILs are generally more expensive than common solvents, detailed engineering design taking into account their unique properties could reveal unforeseen process benefits and improvements that offset their costs.

4.1. Alternative solvents for CO_2 absorption processes

It has been suggested that the use of ILs as alternative solvents would have many advantages over conventional amine-based CO_2 absorption.[8] In addition to a potential lower energy demand for regeneration, ILs also have negligible vapor pressure, which reduce the environmental concerns regarding their use as solvents in CO_2 absorption processes when compared to amines.

A great deal of effort has been put on the experimental determination and theoretical understanding of gas solubilities in ILs.[65-69] For example, the CO_2 solubilities in several commonly used ILs have been carefully studied and some general trends were observed.[70-75] The influence of different functional groups, such as alkyl, ether, hydroxyl, nitrile and fluorine, on the gas solubility properties of ILs has also been intensively investigated.[76-80] It was found that increasing the

cation alkyl side length increases the CO_2 solubility, likely by increasing the available volume for CO_2 molecules due to a decrease in cation-anion interactions.[74, 75] Also, it was observed that the anions of ILs have a stronger influence on CO_2 solubility,[62, 65] and that the CO_2 molecules have a larger affinity for anion *versus* cation associations.[71] The anion effect on CO_2 solubility was also investigated through molecular dynamics,[70] and the anion-CO_2 interactions were shown to be the strongest solvation forces present. The bis(trifluoromethylsulfonyl)imide ($[NTf_2]^-$) anion generally exhibits the best CO_2 selectivity and have high overall CO_2 solubility.[62, 65] Fluorination of the cation and/or the suitable choice of the anion can effectively improve the CO_2 solubility in conventional ILs, but at this stage they still cannot compete with the current technology due their lower CO_2 capacities. In view of that, task-specific ILs for chemisorption have also been developed.

In contrast to conventional ILs, which mostly use physical absorption to capture CO_2 into the spaces between ions, task-specific ILs are designed to additionally have chemisorption by introducing suitable moieties (like amines) to chemically bond the CO_2 and increase the overall absorption capacity. Bates *et al*.[81] proposed a task-specific IL consisting of an imidazolium cation with a primary amine moiety covalently tethered for CO_2 capture and studied the reaction mechanism. The incorporation of amines groups into either the cation or the anion generally provides strong complexation with CO_2 molecules, allowing for chemisorption at the stoichiometric ratio of 2:1 (IL : CO_2). Unfortunately, these ILs generally have low thermal stabilities and higher viscosities than conventional ILs,[82] and consequently different functionalization strategies have been recently explored.[83-85] The high diversity of task specific ILs studied up to now is clearly seen throughout the several studies available in literature. The most recent works focus on ILs containing basic anions, such as carboxylates,[86-89] amino acids,[90, 91] imidazolide, pyrrolide or triazolide.[92, 93]As all these works showed that the high

synthetic flexibility of ILs allows for the design of a broad range of different solvents with high CO_2 capacities, the cost and the stability of these ILs also become important considerations. Thus, additional research should be carried out on this topic in order to improve their competition with the traditional solvents.

4.2. Emerging materials for CO_2 separation membranes

Ionic liquids can be used in various morphologies and configurations as membranes. The simplest approach is as supported ionic liquid membranes (SILMs), where the desired IL is immobilized into the pores of a solid polymer membrane by capillary forces (Figure 7).[94] SILMs are considered a very attractive approach compared to bulk-fluid ILs since much smaller amount of IL is needed. On the other hand, their negligible vapor pressure eliminates one of the problems associated with traditional liquid membranes, namely liquid volatility.[95]

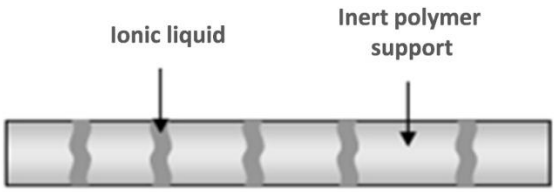


Figure 7| Schematic representation of a supported ionic liquid membrane (SILM).

A broad diversity of ILs has already been used to develop SILM systems. Several authors have investigated the effect of the IL structure, covering diverse cations, such as imidazolium,[96-114] pyrrolidinium,[113, 115, 116] phosphonium,[117-120] pyridinium,[74, 116] ammonium,[121-123] or thiazolium,[124, 125] combined with halogens, fluorinated anions, sulfonates, carboxylates, amino acids, and cyano-containing anions. In line to what was found for bulk-fluid ILs, the results obtained using SILMs showed that the anions usually have stronger influence than cations on the CO_2 separation performance of these membranes.[94] In particular, the results also

indicated that cyano-containing anions promote not only increased CO_2 permeabilities, but also enhanced CO_2/CH_4 and CO_2/N_2 selectivities when compared to the $[NTf_2]^-$ anion.[106]

Other studies, mainly focused on imidazolium-based ILs, explored different structural variations of the cation in order to enhance the CO_2 selectivity of SILMs. Carlisle *et al.* demonstrated that the introduction of a nitrile group in the imidazolium cation improves the CO_2/N_2 selectivity.[78] Bara *et al.* functionalized imidazolium-based ILs with oligo(ethylene glycol) and they observed that the CO_2/N_2 and CO_2/CH_4 solubility selectivities of these ILs are higher than those of their corresponding alkyl analogues.[126] The same authors also found that fluoroalkyl groups attached to the imidazolium cation can enhance the CO_2 permeability relative to CH_4, whereas the fluoroalkyl interactions with N_2 reduce the CO_2/N_2 permselectivity.[127] Furthermore, SILMs using task-specific ILs with amines groups either in the cation or anion for facilitated CO_2 transport were also proposed.[128-132] Most of the representative successes and failures to improve the separation performance of SILMs via functionalization and facilitated transport in the context of CO_2/CH_4 and CO_2/N_2 were summarized and discussed by Scovazzo.[94]

It is worthy to note that SILMs have shown good CO_2 separation performances, with permeabilities/permselectivities that are consistently close or above the 2008 Robeson upper bounds for CO_2/CH_4 and CO_2/N_2,[94] meaning that SILMs are highly competitive with polymer membranes. Nevertheless, the industrial application of SILMs is limited due to their inadequate long-term stability since they are susceptible to failure if the pressure differential across the membrane is high enough to push out the IL phase from the pores of the membrane support. Actually, SILM stability is still an open issue as different behaviors have been found depending on the nature of both the IL and the membrane support, as well as on the pore size.[133-135]

In order to overcome the limitation inherent to SILMs, research has been carried out on the fabrication of CO_2 separation membranes using ILs through three different approaches, namely: (i) polymer–IL composite membranes, (ii) gelled IL membranes and (iii) polymerized IL–based membranes.

The first approach has explored the blending of ILs with polymers to make homogeneous composite membranes.[136-143] Although these composite materials have shown enhanced mechanical strength and favorable gas transport properties, a limiting working pressure difference across the membrane was also observed. Given that the IL is entrapped in the tight spaces between the polymer chains, there is no chemical bonds tethering the IL to the polymer, and consequently high pressure differentials compress the membrane and can cast out the IL.

The second approach to design membranes making use of ILs is the formation of gelled structures using either low-molecular weight gelators or compatible macromolecules.[144-151] Gelled IL membranes have improved mechanical properties and exhibit higher burst pressures compared to SILMs, while the solubility characteristics remain very similar to those of ILs. Gelation is a suitable method for preparing pseudo-solid membranes with gas transport properties close to pure ILs and polymer-like mechanical stability. However, the CO_2 permeance of the gelled IL membranes prepared so far is limited by their thickness, and thus the use of a support reduces their CO_2 separation efficiency.

Alternatively, and considering that ILs present a unique platform for monomer design, where functional groups can be easily introduced for a specific application, the third and most promising way to take advantage of ILs for CO_2 separation and simultaneously overcome the inherent disadvantages of the previous two approaches is to polymerize IL monomers and prepare solid polymer membranes.[95] Taking into consideration that the majority of the research work presented in this dissertation makes use of polymeric ionic liquids to design CO_2

separation membranes, the progress and scientific results obtained using this approach are thoroughly revised in the next section.

5. Polymeric Ionic Liquids (PILs)

Polymeric ionic liquids or poly(ionic liquid)s, are a subclass of polyelectrolytes that comprise IL species connected through a polymeric backbone to form a macromolecular architecture.[152-155] Some of the remarkable IL features, particularly the unique tunability of their physical and chemical properties, are incorporated into the polymer, opening the door to the creation of a new platform for the development of advanced polymeric materials.

The concept behind the definition of PILs is solely based on how they are generated by the (formal) polymerization of an IL monomer in which one or more polymerizable units are incorporated (Figure 8 (a)).[155] The polymerizable group of an IL monomer can be located either on the cation or the anion, depending on the desired polymeric architecture. In addition, IL monomers with two polymerizable units can be used to build up more complex PIL networks (Figure 8(b)).[154]

The development of PILs has been following the initial trends of ILs, where counter-anions containing halides or fluorine atoms and polycations cations bearing imidazolium,[156-158] pyridinium,[159] piperidinium,[160] pyrrolidinium,[160, 161] or ammonium moieties,[159] were the first to be synthesized by conventional free radical polymerization of IL monomers or via chemical modification of existing polymers. A few years ago, when the first comprehensive reviews on PILs came out,[152-154] these polymers most prominent applications dealt with their conductivity and self assembly properties as ionic conductors in electrochemical devices,[162-164] dispersants and stabilizers,[165-168] sensitive materials,[169, 170] or precursors for carbon materials.[171, 172] Nowadays, PILs are being researched in terms of the tunability of their affinity properties and recent applications across diverse fields are being established, namely in gas separation and water

purification membranes,[173, 174] analytical chemistry,[175] thermoresponsive materials,[176] energy,[177] and for bio-related applications.[178] This shift in interests is mainly due to the development of newly original PIL chemical structures, where the recent advances in the preparation of PILs by controlled/living radical polymerization techniques,[155] as well as the introduction of new types of cations and anions from the IL area,[178-181] are broadening the access to precisely designed IL species within a polymer matrix for each specific purpose.

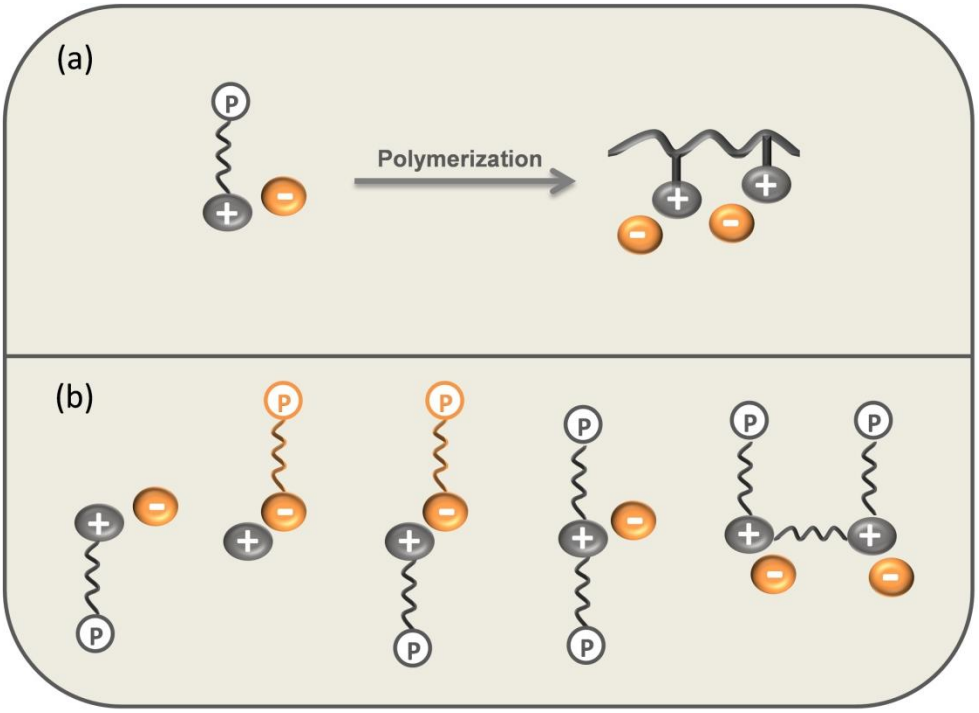


Figure 8| Schematic illustration of (a) polymerization of IL monomer and (b) basic IL monomers. Note that "p" represents a polymerizable group.

5.1. PILs as CO_2 sorbents

Although pioneering studies anticipated the use of PILs as advanced polymer electrolytes,[182-185] a number of studies have been carried out to investigate CO_2 sorption in PILs.[186-196]

In 2005, Radosz and coworkers first reported the study of CO_2 absorption by imidazolium-based PILs combining tetrafluoroborate $[BF_4]^-$ or hexaflourophosphate $[PF_6]^-$ anions and showed that those materials exhibit even higher CO_2 absorption capacity and faster absorption/desorption rates than the corresponding ILs.[186, 187] Later, the same group demonstrated that ammonium-based PILs have higher CO_2 sorption capacity than the imidazolium-based ones.[188] It was also observed that the CO_2 sorption properties of pyrrolidinium-based PILs are significantly affected by the nature of the counter-anion.[193]

More recently, a series of PILs based on polyurethane, a versatile and low-cost material, were synthesized and their CO_2 sorption behavior was evaluated under different pressures.[197] In view of the fact that better CO_2 sorption performances were obtained compared to other PILs described in literature, this work highlighted that the presence of nitrogenated and polyether structures allied to the imidazolium ring in the PIL backbone might be promising for CO_2 capture.[197]

5.2. PIL-based membranes for CO_2 separation

As a versatile and tunable platform for designing a broad range of different polymer chemical structures, PILs are emerging as alternative materials to improve existing membrane-based CO_2 separation processes. Noble's group first established their potential with CO_2/CH_4 and CO_2/N_2 permeability selectivities on par or greater than those observed for conventional SILMs.[198-201] Even though PILs afford solid stable membranes, their major drawback is the substantial drop in

both gas permeability and diffusivity when compared to those of their IL analogues in SILMs. To this end, different strategies have been investigated for designing robust PIL-based membranes with improved performances (Figure 9).

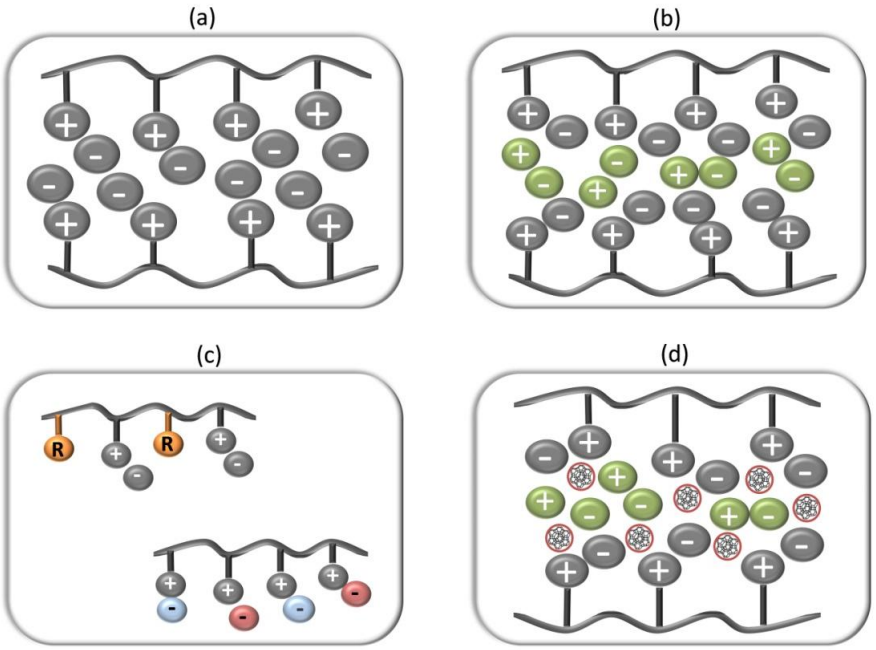


Figure 9| Schematic illustration of (a) neat PIL membrane (b) PIL–IL composite membrane, (c) PIL copolymer membranes, (d) PIL–IL–zeolite mixed matrix membrane.

The following subsections cover the advances on the design of PIL-based membranes for CO_2 separation, in particular for flue gas separation (CO_2/N_2) and natural gas purification (CO_2/CH_4). The evaluation of gas permeation properties, as well as CO_2 separation performances obtained during the progressive development of these membranes will be here discussed. As illustrated in Figure 9, four different strategies will be highlighted: (i) neat PIL membranes having different functional groups attached to their imidazolium-based backbones,[198-204] (ii) the blending of free ILs with PILs to form homogeneous composite membranes,[202-209] (iii) synthesis of PIL copolymers to control segmental motion

and chain packing for increasing the gas permeability and mechanical stability of the membranes,[173, 210-213] and (iv) the incorporation of zeolites into PILs to form mixed matrix membranes.[214-216]

(i) Neat PIL membranes

The potential performance of PILs as gas separation membranes was initially addressed in 2006 by Camper *et al*.[198] Using CO_2, CH_4 and N_2 solubility data and taking into account the solution-diffusion mass transfer mechanism, permeabilities of immobilized ILs were predicted by lowering the gas diffusion coefficients by subsequent orders of magnitude, in a trial and error manner. The authors postulated that if solubility remains the same, the performance of those hypothetical stabilized IL membranes would be promising for CO_2 separations.[198] The best way to "make those membranes come true" was to use polymerizable IL monomers to prepare neat PIL membranes (Figure 9(a)). The radical chain-addition polymerization of IL monomers combining a polymerizable group is the most commonly used route to prepare PILs, which can be easily converted into dense polymer membranes. The chemical structures of the neat PILs synthesized so far to prepare CO_2 separation membranes are shown in Figure 10. Among the PILs used, all comprising imidazolium cation moieties in their polymeric backbones, the most studied combine the $[NTf_2]^-$ as counter-anion.

The first neat PIL membranes for CO_2 separation were presented by Noble's group.[199] Five PILs featuring alkyl-imidazolium cations tethered to a polystyrene (**PIL 1a-c**) or polyacrylate backbone (**PIL 2a,b**) were synthesized by UV polymerization using a photo-initiator and a cross-linking agent, and subsequently the CO_2, CH_4 and N_2 permeation properties of the prepared neat PIL membranes were evaluated. The chemical structure of the polymer backbone had little effect on the gas permeation properties of the membranes, whereas both the permeability of all gases and the CO_2 permselectivity were largely dependent of

the alkyl chain length attached to the imidazolium polycation.[199] For instance, the CO_2 permeability increased from 9 to 32 Barrer as the alkyl group was lengthened from methyl to hexyl in the styrene-based systems (**PIL 1a-c**), but their permselectivities for CO_2/N_2 decreased from 32 to 28, and for CO_2/CH_4 from 39 to 17.[199] The CO_2 separation performances of this first generation of neat PIL membranes are shown in the form of Robeson plots in Figure 11.

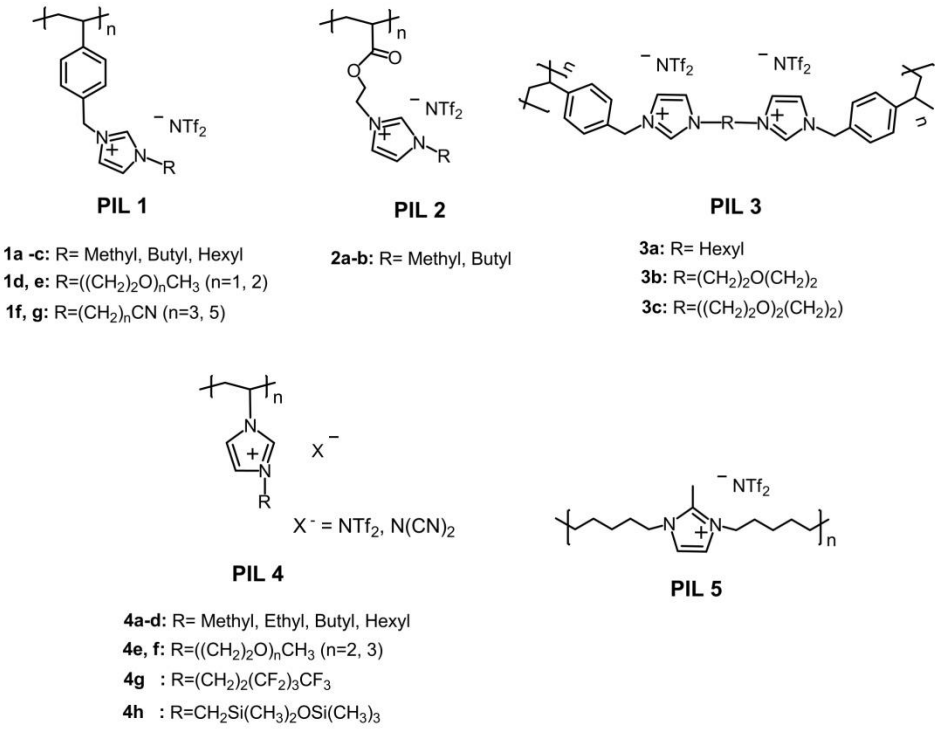


Figure 10| Chemical structures of cationic PILs that have been evaluated as CO_2 separation membranes.

In order to improve the CO_2 separation performance of these membranes, Noble and co-workers proposed a second generation of functionalized imidazolium-based PILs containing polar groups, namely oligo(ethylene glycol) (**PIL 1d,e**) or alkyl-terminated nitrile (**PIL 1f,g**).[200] The inclusion of pendant nitrile groups decreased the CO_2 permeabilities (4 – 8 Barrer), while PILs combining

oligo(ethylene glycol) units exhibited CO_2 permeabilities (16 – 22 Barrer) that were on par with their alkyl analogues (9 – 32 Barrer).[200] As it can be seen in Figure 11, these functionalized PILs (**PIL 1d,e** and **PIL 1f,g**) generally have improved CO_2/N_2 (37 to 44) and CO_2/CH_4 (29 to 37) permselectivities when compared to those with alkyl chain substituents (**PIL 1a-c**).[200]

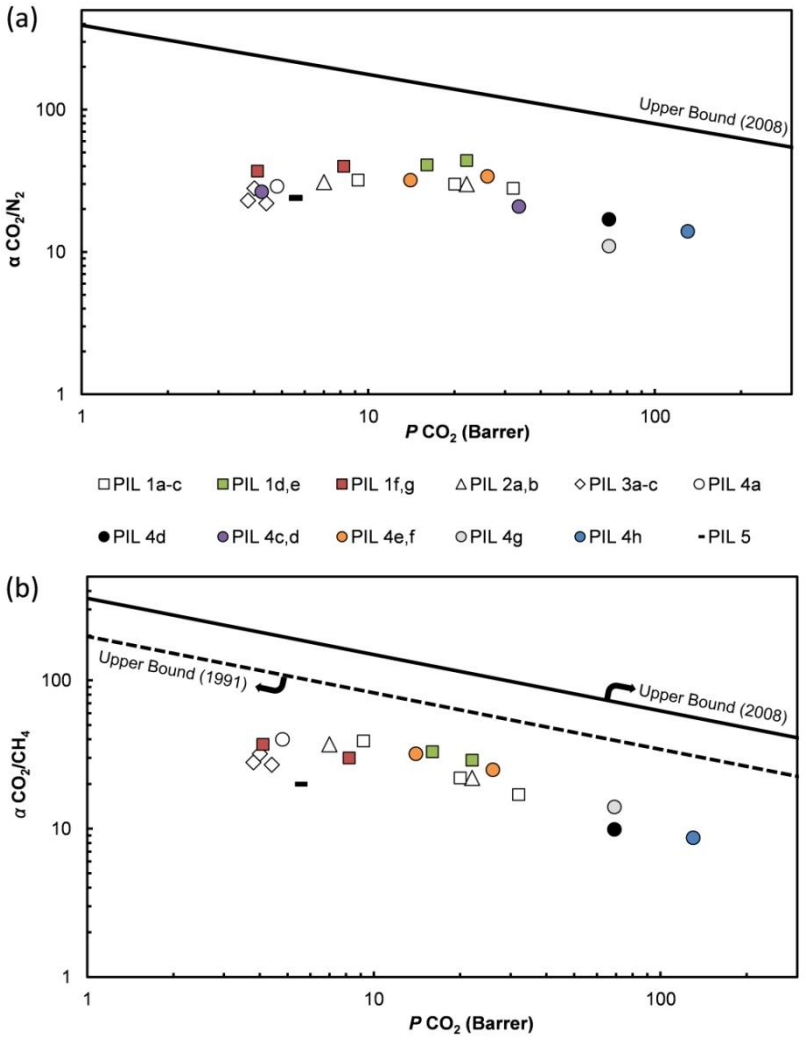


Figure 11| CO_2 separation performance of the neat PIL membranes plotted on (a) CO_2/N_2 and (b) CO_2/CH_4 Robeson plots. Data from References[198-204] are plotted on a log-log scale and the upper bounds for each gas pair are adapted from Robeson.[43, 44]

Cross-linked PIL membranes with different spacer groups (**PIL 3a-c)** were also synthesized from the corresponding multifunctional styrene IL monomers.[201] However, this approach is less successful to prepare PIL membranes due to their highly cross-linked structures. Although these membranes exhibited similar CO_2/N_2 (22 – 28) and CO_2/CH_4 (22 – 28) permselectivities, the obtained CO_2 permeabilities through the cross-linked PIL membranes were significantly lower (3.8 – 4.4 Barrer)[201] compared to those observed in the imidazolium-based PILs previously studied.

In addition to polystyrene and polyacrylate backbone-based PILs, several PILs featuring functionalized imidazolium cations tethered to a polyethylene backbone (**PIL 4a-h**) have also been tested. Considering that vinylimidazolium monomers are easier to synthesize than their styrene analogues, Carlisle *et al*.[202] evaluated the gas permeabilities and CO_2 separation performance of six vinylimidazolium-based PILs (**PIL 4a** and **PIL 4d-h**) combined with the $[NTf_2]^-$ anion. The results showed that the primary factor differentiating CO_2 permeability in **PIL 4a** from both **PIL 1a** and **PIL 2a** was its diffusivity, which suggests that **PIL 4a** possesses a much rigid polymer matrix.[202] PIL having disiloxane functionalized vinylimidazolium cation (**PIL 4h**) was found to be the most CO_2 permeable membrane (130 Barrer), although less selective (CO_2/N_2 = 14, CO_2/CH_4 = 8.7).[202] Conversely, fluoroalkyl substituents (**PIL 4g**) contributed only to a slight increase in the CO_2/CH_4 permselectivity, without changing the CO_2 permeability (Figure 11). Furthermore, Li *et al*.[203] synthesized three new alkyl functionalized vinylimidazolium-based PIL using $[N(CN)_2]^-$ as counter-anion (**PIL 4b-d**). Likewise, Bara *et al*.[199] previously observed for styrene and acrylate backbone-based PILs, increasing the alkyl chain substituent from ethyl to hexyl in the vinylimidazolium-based systems, increased the CO_2 permeability but reduced the CO_2/N_2 permselectivity of the membranes.[203] Even though PILs with $[N(CN)_2]^-$ as counter-anion were less CO_2 permeable (0.09 – 33.5 Barrer) than their corresponding analogues with the

$[NTf_2]^-$ anion, the authors observed that **PIL 4d** with $[N(CN)_2]^-$ presents higher CO_2/N_2 permselectivity (21) than that of **PIL 4d** with the $[NTf_2]^-$ anion (17).

Main-chain cationic PILs (**PIL 5**) have also been developed by Noble's group.[204] In this case, the imidazolium functionality is located in the main polymer backbone between alkyl spacers instead of within the side groups, and consequently endorses a different polymer architecture.[204] In Figure 11, it can be observed that **PIL 5** does not significantly outperform the PIL membranes previously tested for CO_2/N_2 and CO_2/CH_4 separations. In fact, the permselectivity of **PIL 5** (CO_2/N_2 = 24, CO_2/CH_4 = 20) is in the same range of most imidazolium-based PILs with side chains, but its CO_2 permeability (5.3 Barrer) lies in the least permeable neat PIL membranes area.[204]

At this stage, it is evident that functionalization of the imidazolium-PIL polycation alone cannot promote the large improvement in gas permeability required for neat PIL membranes to be technologically competitive. Nevertheless, the knowledge gained from these studies, particularly regarding structure-properties relationships, was undoubtedly a necessary step for the development of improved PIL-based membranes.

(ii) PIL–IL composites

The major factor retarding the gas transport through PIL membranes compared to SILMs, is the large decrease in both gas permeability and diffusivity through the solid polymer matrix. Actually, an ideal membrane should combine adequate CO_2 permeability and permselectivity of a SILM with the mechanical stability and robustness of a polymer. The low gas permeabilities in neat PIL membranes encouraged Noble's group to re-examine the role of ILs in CO_2 separation membranes, this time by incorporating them in PILs. This concept started as a way to achieve membranes with higher gas permeabilities while maintaining their mechanical stability. ILs within PILs are different from traditional plasticizers in

conventional polymers due, not only to their negligible vapor pressure,[47] but also to their ability to strongly interact with the charged PIL backbone through electrostatic interactions. This means that the large degree of electrostatic forces holding the IL within the PIL matrix should not be overcame by applied pressure. A schematic illustration of PIL–IL composite membranes is shown in Figure 9(b). The chemical structures of several PILs and ILs, which have been used to prepare composite membranes, are shown in Figures 10 and 12, respectively.

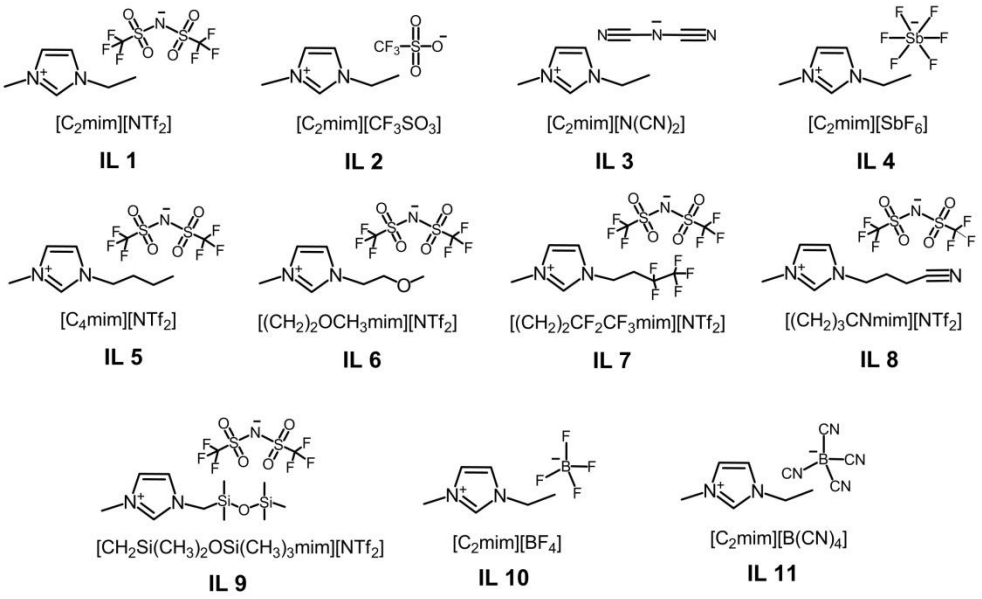


Figure 12| Chemical structures and short names of the ionic liquids used to prepare PIL–IL composite membranes.

The proof-of-concept for PIL-IL composite membranes for gas separation was published by Bara *et al.*,[205] who prepared solid stable PIL–IL composite membranes by the polymerization of an IL monomer in the presence of a non-polymerizable IL (also called "free IL"). The incorporation of 20 wt% of free **IL 1** into **PIL 1a** increased its CO_2 permeability by approximately 400% compared to the neat **PIL 1a** membrane, while permselectivities of 39 for CO_2/N_2 and 27 for

CO_2/CH_4, were obtained, with differences of 33% and minus 25%, respectively.[205] Afterwards, Bara *et al*.[206] also changed the anion of the free IL component. They combined the **PIL 1d** with 20 wt% of free imidazolium-based ILs having different anions (**IL 1-4**). The composite membrane containing 20 wt% of free $[C_2mim][NTf_2]$ (**IL 1**) exhibited the highest CO_2 permeability (60 Barrer) compared to the other prepared composites (which varied from 41 to 43 Barrer). Owing to the fact that $[C_2mim][NTf_2]$ has the largest molar volume, a composite membrane with higher free volume was prepared, allowing for a faster gas diffusion.[206] What is more, CO_2/N_2 (36 – 39) and CO_2/CH_4 (24 – 27) permselectivities of the PIL–IL composites, are only slightly smaller than those of the neat **PIL 1d** membrane (CO_2/N_2 = 41, CO_2/CH_4 = 33), meaning that only a minimal permeability/permselectivity tradeoff exists for these membranes (Figure 13). In the same line of research, Bara *et al*.[207] assessed the effect of functionalized imidazolium cation species of the free IL constituent. Imidazolium-based ILs containing alkyl, ether, fluoroalkyl, nitrile and siloxane groups (**IL 5-9**) were incorporated again into **PIL 1d**. For composites containing alkyl, ether and fluoroalkyl groups similar CO_2 permeabilities (47-53 Barrer) and permselectivities ($CO_2/N_2 \approx 37$ and $CO_2/CH_4 \approx 26$) were obtained.[207] The composite bearing the nitrile groups attached to the free cation displayed the highest CO_2/N_2 (40) and CO_2/CH_4 (28) permselectivities, but also the smallest CO_2 permeability (33 Barrer). Conversely, the PIL–IL composite membrane with siloxane functionality is the most permeable, with a CO_2 permeability of 55 Barrer, but it exhibited the smallest CO_2/N_2 (33) and CO_2/CH_4 (20) permselectivities.[207]

The large gas permeability improvements obtained by the incorporation of free IL into PILs inspired more researchers to pursue this approach. Li *et al*.[208] synthesized a series of PIL–IL composites with a concentration of free IL ranging from 15 to 60 wt%. They showed that the incorporation of **IL 5** into **PIL 3** caused an increase in the free volume of the membranes. However, it was observed that increasing the amount of free **IL 5** into **PIL 3c** enhanced the CO_2 and N_2

permeabilities, solubilities and diffusivities, but did not significantly affect the CO_2/N_2 (22-26) permselectivities of the composites.[208] The composites were found to be stable under transmembrane pressure differential of 10 bar.[208] Later, the same group[203] evaluated the performance of PIL–IL composites based on alkyl functionalized vinylimidazolium-PILs with $[N(CN)_2]^-$ as counter-anion (**PIL 4b-d**). These PILs were blended with different free ILs, namely $[C_2mim][N(CN)_2]$ (**IL 3**), $[C_2mim][BF_4]$ (**IL 10**), and $[C_2mim][B(CN)_4]$ (**IL 11**), which were chosen due to their high CO_2/N_2 separation performance.[106] In this case, the incorporation of the free ILs not only significantly increased the CO_2 permeability but also enhanced the CO_2/N_2 permselectivity.[203] The best CO_2 separation performances were achieved for the composites of **PIL 4c** with 66.6 wt% of **IL 3** and **IL 11,** presenting CO_2 permeabilities of 273 and 340 Barrer and CO_2/N_2 permselectivities of 51 and 39, respectively.[203] As it can be seen in Figure 13(a), these two PIL–IL composite membranes have CO_2/N_2 separation performance very close to the Robeson 2008 upper bound, suggesting their enormous potential for post-combustion flue gas treatment.[203]

Carlisle *et al.*[209] used a different approach that consists on the preparation of cross-linked PIL–IL gel membranes. These authors prepared a series of membranes by photopolymerization of oligo(ethylene glycol) functionalized cross-linking and non cross-linking vinylimidazolium IL monomers in the presence of free **IL 1**. The effect of the cross-linker content, as well as the free IL loading on the CO_2 separation performance of these membranes was investigated. The CO_2 permeability was dramatically increased at the three concentrations (45, 65, 75 wt%) of IL loading, while both the CO_2/N_2 and CO_2/CH_4 permselectivity remained nearly constant.[209] The gas diffusivity through the membranes can be increased by decreasing the cross-linker concentration.[209] These cross-linked PIL–IL gel membranes are quite promising since this configuration can stabilize 75 wt% of free IL while presenting "liquid-like" CO_2 separation performance, with CO_2

permeability of 520 Barrer and good CO_2/N_2 and CO_2/CH_4 permselectivities of 37 and 20, respectively.

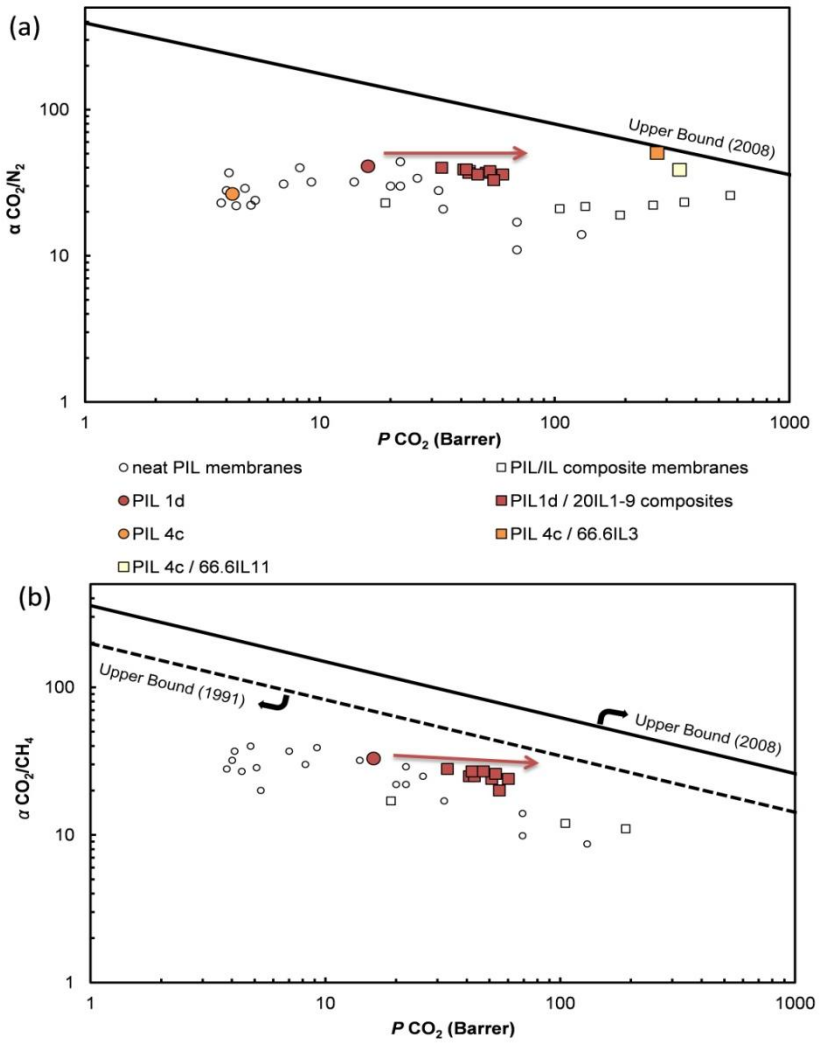


Figure 13| CO_2 separation performance of the PIL–IL composite membranes plotted on (a) CO_2/N_2 and (b) CO_2/CH_4 Robeson plots. Data from References[202-209] are plotted on a log-log scale and the upper bounds for each gas pair are adapted from Robeson.[43, 44]

In summary, all these studies demonstrate that by the addition of free IL enables the increase in the CO_2 permeability of PIL-based membranes with little, if

no, sacrifice of their CO_2 permselectivities. It was also observed that the gas permeation properties of the free IL greatly influence the CO_2 separation performance of the composites and as the amount of free IL increases, the CO_2 separation performance of the composite further deviates from the parent neat PIL and approaches that of the analogous SILM. Consequently, the choice of the appropriate IL is crucial in the tailoring of the PIL–IL membrane properties for improving their CO_2 separation performance.

(iii) PIL copolymer membranes

The synthesis of PIL copolymers that contain at least one PIL monomeric unit has also been attracting great attention[153, 155] since copolymerization is a general strategy to tune the desired properties of macromolecules. Thus, the synthesis of PIL copolymers is an additional and alternative strategy for designing PIL-based CO_2 separation membranes.[173, 210-213] The chemical structures of the PIL copolymers that have been developed for this purpose are shown in Figure 14.

Radosz and co-workers were the first to test PIL copolymers as CO_2 separation membranes.[210] The main objective was to prepare less brittle PIL membranes by grafting poly(ethylene glycol) (PEG) onto glassy ammonium-based PILs to form PIL–PEG membranes (**coPIL 1 and 2**).[210] The resulting membranes were found to be chemically and mechanically stable, with CO_2 permeabilities as high as 40 Barrer (at 308 K) and CO_2/N_2 permselectivities up to 70.[210]

More recently, Li and Coleman[211] synthesized random copolymers having diamino functional IL monomeric units within a block copolyimide backbone (**coPIL 3a,b**) and then prepared free standing membranes by the film casting method. Nonetheless, the incorporation of IL monomeric units reduced the gas permeabilities, solubilities and diffusivities, and fairly increased (4%) the CO_2/CH_4 permselectivity compared to the pure block copolyimide.[211] Furthermore, Chi *et al*.[212] synthesized graft copolymers consisting of poly(vinyl chloride) (PVC) main

chains and imidazolium-based PIL side chains (**coPIL 4a,b**) via atom transfer radical polymerization. The resulting membranes maintained good mechanical properties (lower strength and greater elongation than PVC), the CO_2 permeability increased from 1.7 to 17.9 Barrer while the CO_2/N_2 permselectivity slight decreased (from 29 to 25) as the content of PIL increased.[212] Alkyl imidazolium functionalized poly(ether ketone)s (im-PEKs) were also synthesized by polycondensation.[213] The copolymers combining the pendant imidazolium cations with different alkyl chains (**coPIL 5a-c**) displayed good thermal and mechanical stabilities and showed high CO_2/N_2 permselectivities up to 66. However, the CO_2 permeabilities, between 1.11 and 1.89 Barrer, are very low.[213]

Keeping in mind both the advantages of PILs and the effect of nanostructured, phase-separated block copolymers, Noble's group synthesized a new type of block copolymers (**coPIL 6a-d**) combining an imidazolium-based PIL and an alkyl non-ionic polymer. In this work, Nguyen *et al.*[173] showed that the combined effects of composition and nanostructure of the block copolymers have an important impact on both the CO_2 permeability and CO_2/N_2 permselectivity. For instance, decreasing the IL block amount increased the CO_2 permeability by one to two orders of magnitude up to 9300 Barrer, and simultaneously decreased the permselectivity, since the diffusion of both CO_2 and N_2 are favoured by formation of nanostructures in the "ionic liquid domain".[173] On the other hand, these new block copolymers have distinctive advantages over the analogous pure homopolymers with respect to membrane preparation since they can be successfully fabricated as defect-free, thin (3 – 20 μm) supported membranes.[173]

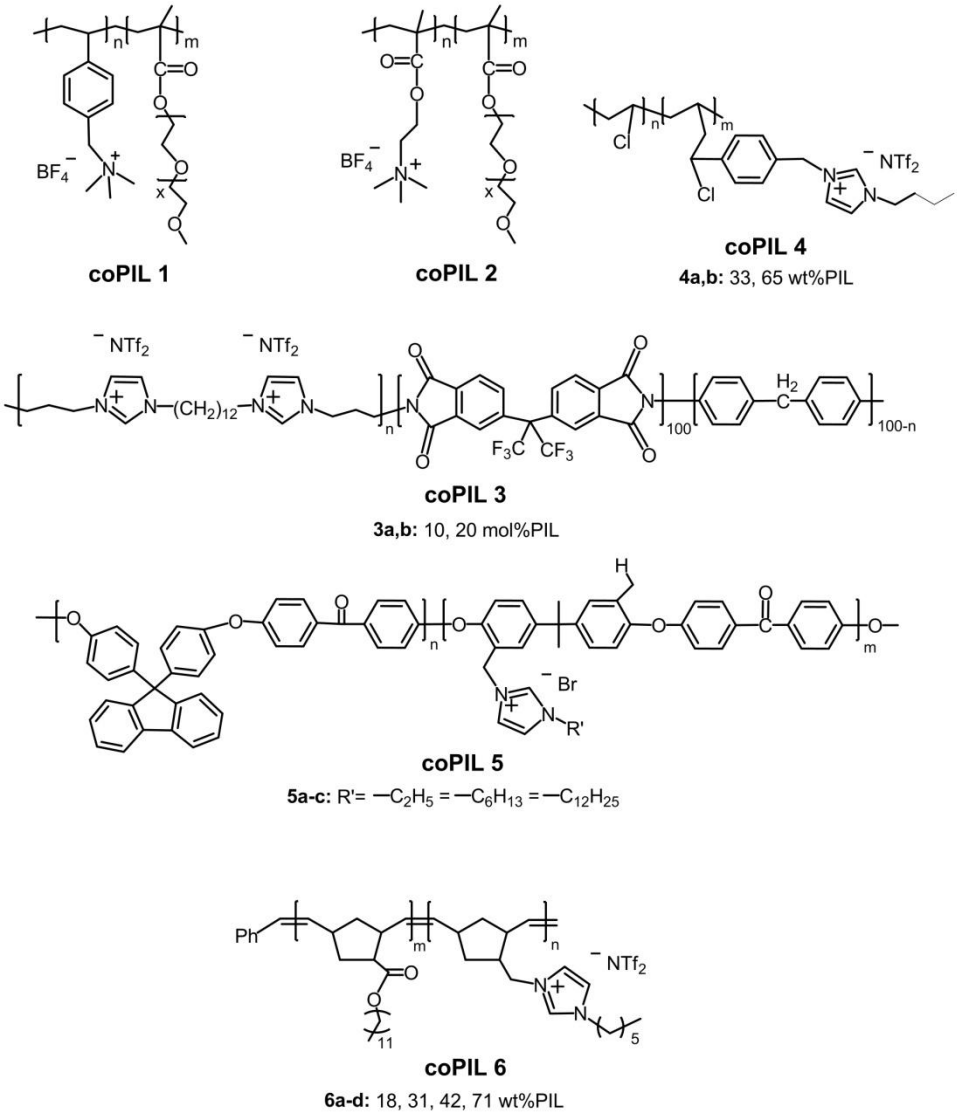


Figure 14| Chemical strucuture of the PIL copolymers that have been evaluated as CO_2 separation membranes.

The CO_2/CH_4 and CO_2/N_2 separation efficiencies of PIL copolymer membranes developed so far are plotted in Figures 15(a) and (b). These membranes do not outperform the Robeson 2008 upper bounds for CO_2/CH_4 and CO_2/N_2 separations, but Figure 15 clearly shows that CO_2 separation performance as a function of

permeability can be tuned by using PIL copolymers. Although considerable research is still required for a complete understanding of the relationship between macromolecular structure and gas permeation properties, these results open new possibilities for designing promising PIL-based CO_2 separation membranes with improved mechanical stability.

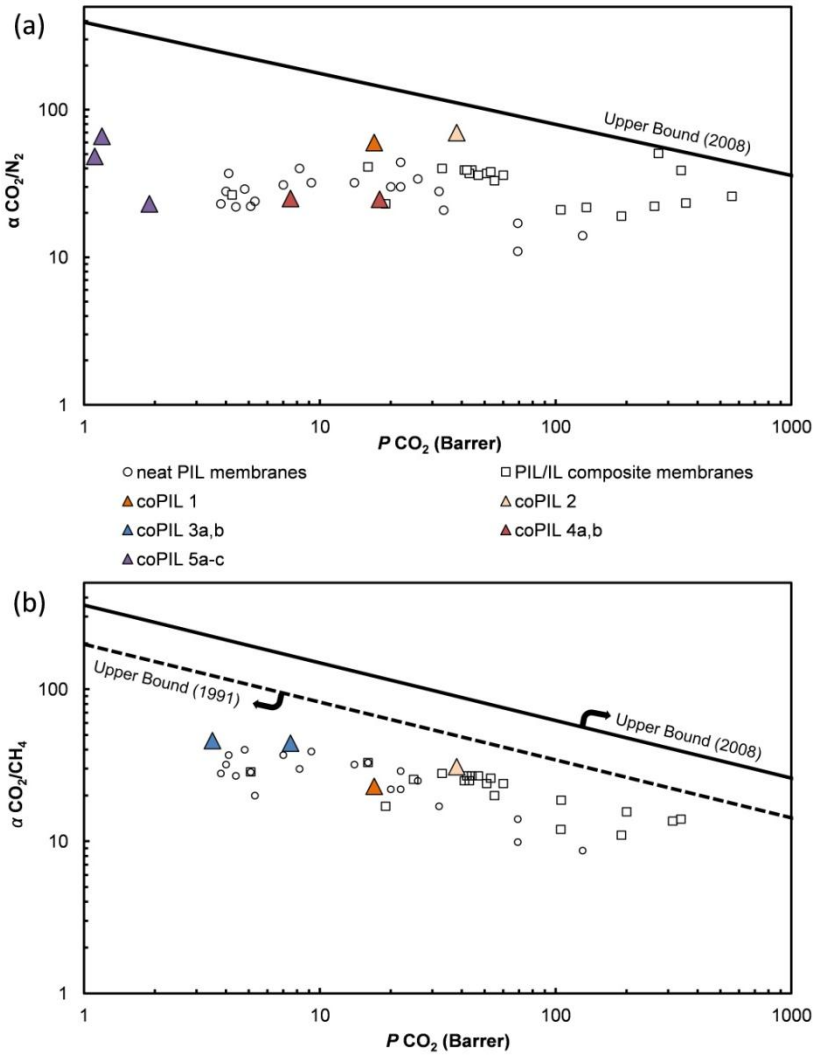


Figure 15| CO_2 separation performance of the PIL copolymer membranes plotted on (a) CO_2/N_2 and (b) CO_2/CH_4 Robeson plots. Data from References[173, 210-213] are plotted on a log-log scale and the upper bounds for each gas pair are adapted from Robeson.[43, 44]

(iv) PIL–IL–zeolite mixed matrix membranes

Mixed matrix membranes have been identified as the potential solution to the tradeoff issues of polymeric membranes,[217] and are normally fabricated by the incorporation of an inorganic solid (dispersed) phase into a continuous polymer matrix. Conceptually, these composite membranes can offer the ease processing inherent to polymeric materials, as well as the enhanced CO_2 permeability and separation performance of inorganic membranes.[33]

In light of the above mentioned aspects, MMMs comprising PIL, free IL and inorganic particles were proposed to improve the CO_2 separation performance of PIL-based membranes.[214-216] The first MMM containing three components of **PIL 1a** (Figure 10), **IL 1** (Figure 12) and zeolite SAPO-34 was studied in 2010 by Hudiono *et al*.[214] A schematic illustration of these composite membranes is shown in Figure 9(d). The results showed that the IL component not only increased the permeability of the membrane, but also improved the interfacial adhesion between the zeolite and the PIL.[214] The permeability of CO_2, CH_4 and N_2 through the **PIL 1a–IL1**–SAPO-34 membrane increased by 65%, 50%, and 48%, respectively, compared to that of the respective PIL–IL composite. The incorporation of SAPO-34 zeolites also increased both the CO_2/N_2 and CO_2/CH_4 permselectivities by roughly 11%. However, the performance of PIL–IL–SAPO-34 membrane is still below the upper limit (2008) on the Robeson plots for CO_2/N_2 and CO_2/CH_4 separations.[214] Nevertheless, this pioneer work demonstrated that is possible to improve the organic-inorganic adhesion in a MMM by the addition of free IL, allowing for the fabrication of membranes without defects that are typical to MMMs. Later, Hudiono *et al*.[215] presented a detailed study of the CO_2 separation performance of three-component MMMs focusing on the effect of varying both SAPO-34 and free IL loadings. These results showed how the system can be tuned.

Recently, Hao *et al*.[216] synthesized PIL–IL–ZIF-8 composite membrane using **PIL 4c** (Figure 3), free **IL 1**, **10** and **11** (Figure 5) and different amounts of ZIF-8 (0, 10, 20 and 25 wt%). The prepared membranes exhibited a continuous increase in the CO_2, CH_4 and N_2 permeabilities with increasing ZIF-8 loading in the presence of the three free ILs tested. Nevertheless, a slight decrease in CO_2/N_2 and CO_2/CH_4 permselectivities was also observed, since the ZIF-8 has intrinsically low CO_2 selectivity [216]. For instance, the CO_2 permeability of **PIL 4c–IL11** jumped from 365 to 1062 Barrer, about a three-fold increment, with the incorporation of 25 wt% of ZIF-8, while the CO_2/N_2 and CO_2/CH_4 permselectivities dropped from 30 to 24 and from 16 to 12, respectively.

Even though the CO_2 separation performance of the PIL–IL–zeolite mixed matrix membranes prepared until now has not yet surpassed the 2008 upper bound on the Robeson plots for CO_2/N_2 and CO_2/CH_4 separations, the three studies described above show that fully heterogeneous membranes embedding inorganic particles uniformly can be prepared using both PILs and ILs. In addition, MMMs are currently considered one of the most promising classes of materials for advancing the current membrane gas separation technology, as well as the inherent brittleness problems found in inorganic membranes. Therefore, MMMs based on PILs constitute a highly interesting approach that deserves to be deeply explored.

6. Objectives

Taking into account the extremely broad range of chemical and structural possibilities of IL chemistry, and the undeniable economical and engineering advantages of membrane technology, the main objective of the present dissertation is to contribute to the development of new highly efficient dense membranes based on ILs and their polymers for gas separations with particular focus on CO_2 separation.

To achieve this goal, this thesis explores the development of tailor-made membranes for specific gas applications according to the following steps: (1) synthesis and characterization of new ILs and PILs; (2) preparation of suitable dense membranes by implementing straightforward strategies; (3) Determination of gas permeation properties and evaluation of gas separation performances. The results are expected to be innovative and capable of unraveling specific structure-relationship properties of membrane materials with new functionalities never explored.

7. Thesis Outline

This thesis is divided into nine chapters, following the research work performed during this PhD project. The present chapter introduces this thesis.

In Chapter 2, the use of true biodegradable ILs as liquid phases in SILMs is proposed. Accordingly, four SILMs based on ILs combining the cholinium cation and four different anions belonging to the carboxylic acid family were prepared and their CO_2, CH_4, and N_2 permeation properties were measured. A comparison between the CO_2/CH_4 and CO_2/N_2 permselectivities obtained in this study with those of other SILMs taken from literature is also provided and the major advantages/disadvantages of using cholinium-based ILs in SILMs for CO_2 separation are discussed.

With the purpose of increase the flexibility in tailoring the permeability and permselectivity of SILMs for CO_2 separation, Chapter 3 explores the use of IL mixtures. First, SILMs based on IL mixtures containing a common imidazolium cation and anions that have different CO_2 solubility behaviors (chemical solubility: acetate and lactate; physical solubility: dicyanamide, thiocyanate, and bis(trifluoromethylsulfonyl)imide) are presented in Part I. Following the results obtained and the know-how acquired, Part II focuses on SILMs made of IL mixtures containing sulfate and/or cyano-functionalized anions. The gas

permeation properties through all the prepared IL mixtures in SILM configurations are provided, and Robeson plots are used to evaluate and understand the behavior of their CO_2/CH_4 and CO_2/N_2 separation performances. Since generally permeability in SILMs scales with viscosity while selectivity scales with molar volume, the thermophysical properties, namely density and viscosity, of the prepared IL + IL mixtures are also addressed and the main mechanism governing gas transport are discussed.

Chapter 4 presents the study of the CO_2, CH_4, and N_2 permeation properties of five novel PIL–IL composite membranes based on PILs having different cation pendant units, namely imidazolium, pyridinium, pyrrolidinium, ammonium and cholinium, combined with the same counter-anion. The broad goal of this study was to contribute for understanding the gas transport behavior and shows the influence of polycation variation on the CO_2 separation performance of PIL–IL membrane materials.

In order to establish the feasibility of using pyrrolidinium-based materials to prepare CO_2 separation membranes, a comprehensive view of the gas permeation behavior within the whole material range of compositions, from PILs to ILs, encompassing PIL–IL composites, is provided in Chapter 5. Since PIL–IL membranes are blends combining the properties of both PIL and IL, the analysis of the full material range also addressed the role of the IL on the gas permeation properties and CO_2 separation performances of these composite membranes.

The use of PILs with mixtures of counter-anions to tune the CO_2/CH_4 and CO_2/N_2 separation performances of PIL–IL composite membranes by employing a straightforward strategy is explored in Chapter 6. The synthesis and characterization of a new family of PIL random copolymers having pyrrolidinium cation pendant units combined with different counter-anion mixtures is presented. Composite membranes of the pyrrolidinium random copolymers were

prepared and the evaluation of their tensile mechanical properties, as well as their CO_2, CH_4 and N_2 permeation properties, is also provided and discussed.

In Chapter 7, the synthesis and characterization of novel pyrrolidinium-based PILs containing different cyano-functionalized counter-anions is described. The film forming ability of these PILs with different amount of ILs containing similar cyano-functionalized anions was evaluated and the CO_2 and N_2 permeation properties of the prepared PIL–IL membranes are presented and discussed. The potential of the prepared composite membranes for highly efficient post-combustion CO_2 separation is shown throughout the evaluation of their CO_2/N_2 separation performances on the respective Robeson plot using the 2008 upper bound.

Although the main focus of this thesis is the design of new membranes for CO_2 separation, Chapter 8 describes the use of PILs as alternative polymer matrices to prepare improved membranes for light olefin/paraffin. In this work, a new series of facilitated transport membranes composed of a PIL incorporating different compositions of ionic liquid versus a silver salt mixture (IL–Ag^+) was successfully prepared to efficiently separate ethylene (C_2H_4) from ethane (C_2H_6). The effect of the IL content incorporated, as well as the concentration effect of silver ions on the C_2H_6 and C_2H_4 permeabilities, diffusivities and solubilities is also provided to further understand the impact of different membrane compositions on the gas transport. In addition, the ethylene/ethane separation performance of all the prepared membranes is presented and discussed.

In Chapter 9, the foremost results presented in the different chapters are summarized, and the main conclusions are withdrawn and discussed in an integrated way. Possible challenges and perspectives are also presented.

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Chapter 2

Cholinium-based supported ionic liquid membranes: a sustainable route for CO_2 separation

Adapted from: **L.C. Tomé,** D.J.S. Patinha, R. Ferreira, H. Garcia, C.S. Pereira, C.S.R. Freire, L.P.N. Rebelo, I.M. Marrucho, Cholinium-based supported ionic liquid membranes: a sustainable route for carbon dioxide separation, *ChemSusChem*, 2014, **7**, 110 – 113.

The author contributed to the planning and execution of all the experiments described in this chapter, except the ionic liquids' characterization. The NMR, EA, MS and DSC analyses were performed by R. Ferreira and H. Garcia, while the density and viscosity measurements were carried out by D.J.S. Patinha. The author was also involved on the discussion and interpretation of all results, as well as on the preparation of the manuscript.

1. Abstract

Aiming at full sustainability of CO_2 separation processes, a series of supported ionic liquid membranes (SILMs) based on environmental-friendly cholinium carboxylate ionic liquids (ILs) were successfully prepared. Their gas permeation properties were measured and high permselectivities were obtained for both CO_2/CH_4 and CO_2/N_2.

2. Communication

Due to its close connection to global warming, anthropogenic emission of CO_2 is one of the most important environmental challenges of our age. Since the elimination of CO_2 from power plants and natural gas streams are important separation processes, there is a continuing effort to develop appropriate cost-effective technologies. In this context, membrane separation technology represents a viable alternative because it offers fundamental engineering and economic advantages compared to classical processes (adsorption, extraction, distillation, etc.).[1]

Several types of polymeric membranes for CO_2 separation have been developed during the last years,[2] whereas supported liquid membranes have also been widely investigated.[3] In particular, SILMs have recently attracted considerable attention owing to the unique properties of ILs such as negligible volatility,[4] high thermal stability,[5] low flammability,[6] and high CO_2 solubility and selectivity.[7] These properties provide distinctive advantages over organic solvents commonly used in supported liquid membranes.[8] Although a broad diversity of ILs has been already tested for developing SILMs, covering most commonly used cations, such as imidazolium,[9-16] pyrrolidinium,[17] sulphonium,[18] phosphonium,[19, 20] ammonium,[21] or thiazolium,[22, 23] combined with halogens, fluorinated anions, sulfonates and nitrile-containing anions, their ecotoxicity has been until now

overlooked. Recent studies have showed that many of these ions have remarkable toxicities and are poorly biodegradable.[24] The development of new environmental-friendly ILs prepared from renewable materials has received growing attention in the last few years. In particular, cholinium-based ILs have been synthesized through simple and economical procedures.[25-28] Due to their particular features, namely biocompatibility, biodegradability and low toxicity, ILs combining the cholinium cation with non-hazard anions have been tested for diverse applications such as crosslinking agents for collagen based materials,[29] constituents of aqueous biphasic systems,[30, 31] or in the pre-treatment or dissolution of biomass.[32, 33]

Aiming at full sustainability of CO_2 separation processes, and simultaneously keeping high permselectivities, we propose the use of cholinium carboxylates as liquid phases in supported liquid membranes for CO_2 separation. The use of carboxylated anions has been shown to provide high CO_2 solubilities,[34-36] but the use of these true biodegradable ionic liquids to prepare SILMs has never been attempted before. Accordingly, we prepared four SILMs based on such ILs by combining the cholinium cation with four different anions belonging to the carboxylic acid family (Figure 1) and evaluated their CO_2, CH_4, and N_2 permeation properties.

Ionic liquids used in this work, namely cholinium levulinate ([Ch][Lev]), cholinium lactate ([Ch][Lac]), cholinium glycolate ([Ch][Gly]) and cholinium malonate ([Ch][Mal]), were prepared by dropwise addition of the corresponding acid to aqueous cholinium bicarbonate, following an established procedure.[27] The mixtures were stirred at ambient temperature and pressure for 8 h. The resulting products were washed with diethyl ether to remove unreacted acid. Excess of water and traces of other volatile substances were removed first by rotary evaporation, and then by stir-heating under vacuum. The water contents after the drying step were below 0.7 wt%. The chemical structures of the cholinium-based

ILs were confirmed by ^{1}H- and ^{13}C-NMR, electrospray ionization mass spectrometry and elemental analysis (see Supplementary Information for further details). Viscosity and density were also determined in view of the fact that both the viscosity and the molar volume of the IL are key features in the design of SILMs. A detailed description of these data, in the temperature range from 293.15 to 343.15 K, is presented in Supplementary Information (Table S2).

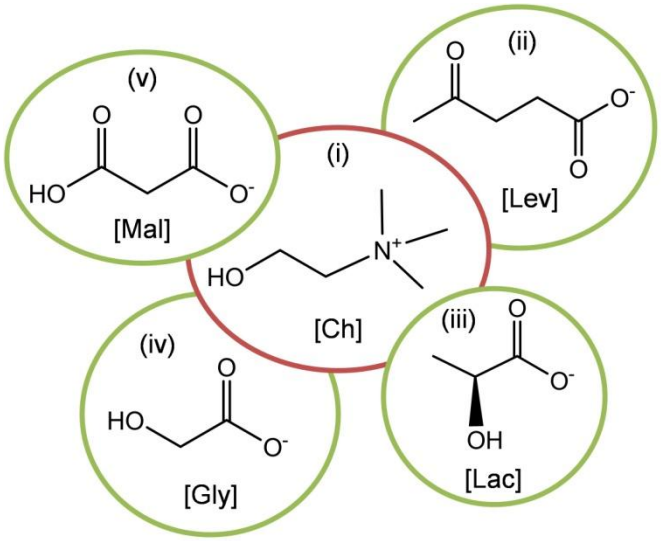

Figure 1| Chemical structures of (i) cholinium cation ([Ch]) and (ii) levulinate ([Lev]), (iii) lactate ([Lac]), (iv) glycolate ([Gly]) and (v) malonate ([Mal]) anions.

The gas permeation properties of the ILs were investigated by using a flat membrane. Porous hydrophilic poly(tetrafluoroethylene) (PTFE) membranes were used to prepare the SILM configurations according to our previously reported procedure.[37] The single CO_2, CH_4, and N_2 permeation properties of cholinium-based SILMs were measured using a time-lag apparatus (details in Supplementary Information), allowing the simultaneous determination of gas permeability and diffusivity. It was also possible to calculate gas solubilities given that the gas transport through a liquid membrane follows a solution-diffusion mechanism where permeability is the product of solubility and diffusivity.[38] Thus, permeability

of the SILMs depends on both thermodynamic and kinetic mechanisms, that is, gas sorption and the gas diffusion, respectively.

Permeabilities and diffusivities of the prepared SILMs toward gases, which were measured at 293 K with a trans-membrane pressure differential of 100 kPa, are shown in Figure 2 and Figure 3, respectively. The CO_2 permeability values vary from 18 to 2 Barrer, while CH_4 and N_2 permeabilities differ from 0.05 to 0.84 Barrer. For all the measured gases, the [Ch][Lev]-based SILM presents the highest gas permeabilities (Figure 2) and diffusivities (Figure 3). This behavior is most likely due to [Ch][Lev] lower viscosity when compared to the other cholinium-ILs studied in this work (see Supplementary Information, Table S2). The permeability of all gases in the cholinium-based SILMs is related to their respective gas diffusivities, with the series from the highest to the lowest permeabilities (Figure 2) being equal to that of diffusivities (Figure 3): [Ch][Lev] > [Ch][Lac] > [Ch][Gly] > [Ch][Mal].

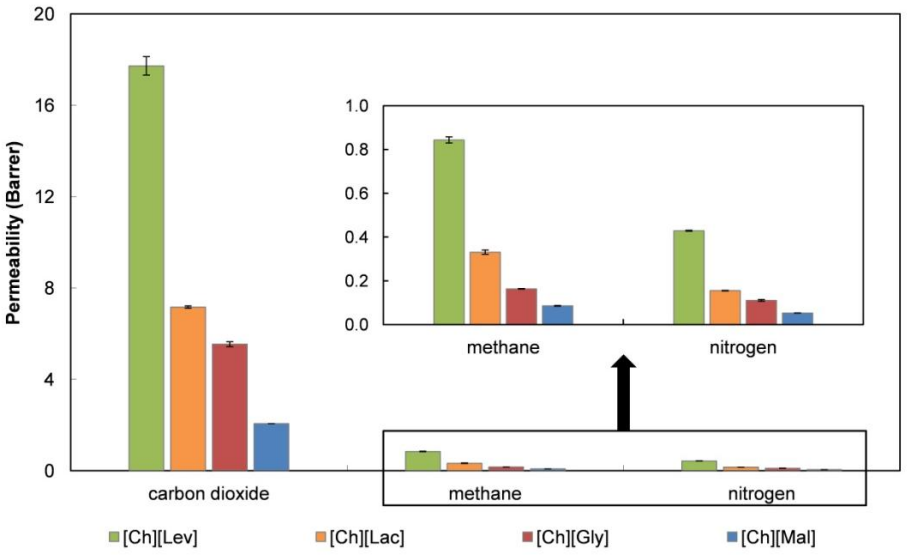

Figure 2| Gas permeability in the prepared cholinium-based SILMs (1 Barrer = 10^{-10} cm^3(STP)cm cm^{-2} s^{-1} $cmHg^{-1}$). Error bars represent standard deviations based on three experimental replicas.

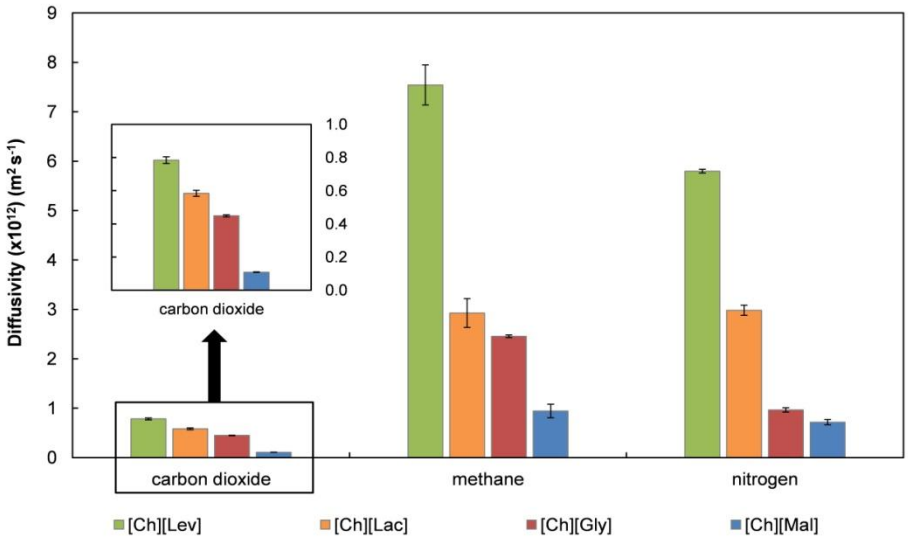

Figure 3| Gas diffusivity in the prepared cholinium-based SILMs. Error bars represent standard deviations based on three experimental replicas.

The cholinium-based SILMs have lower gas permeabilities than imidazolium-, other ammonium- (i.e., different from cholinium), phosphonium- and sulphonium-based SILMs.[18] For example, we showed in a previous study that a SILM made of pure [C_2mim][Lac] has CO_2, CH_4 and N_2 permeability values of 55, 3 and 1 Barrer,[37] whereas the [Ch][Lac]-based SILM reported here has 7, 0.33 and 0.43 Barrer, respectively. One possible reason for these lower gas permeabilities is the high viscosity of cholinium carboxylates when compared to the corresponding imidazolium ILs. In particular, at 293.15 K, the [Ch][Lac] viscosity is 3661.33 mPa s, while for [C_2mim][Lac] is 370.41 mPa s.[37] Higher viscosity hampers gas diffusion through the SILM and consequently reduces the membrane permeability.[18] Our data made apparent that the cholinium carboxylate-based SILMs follow the generally established trend that gas permeability and diffusivity through the SILM decreases as the ionic liquid viscosity increases.

The CO_2, CH_4, and N_2 solubilities calculated in this work are presented in Table 1. For all of the prepared cholinium-based SILMs, the trend obtained for gas permeability (P CO_2 > P CH_4 > P N_2) (Figure 2), was also observed for solubility (S CO_2 > S CH_4 > S N_2) (Table 1). The CH_4 and N_2 solubilities were similar, and significantly lower than that of CO_2, amongst the cholinium carboxylate-based SILMs. These data are in agreement with reported results for other SILMs where usually the CO_2 separation is largely driven by solubility differences between CO_2 and N_2 or CH_4 in the ionic liquids.[18] Conversely, the SILM made of [Ch][Lev] exhibits the highest CO_2 solubility followed by the [Ch][Mal], surpassing the [Ch][Lac] and [Ch][Gly]-based ones. The CO_2 solubilities values of the last two SLIMs are equivalent probably due to similarity of the chemical structures of the $[Lac]^-$ and $[Gly]^-$ anions (Figure 1). It is well known that gas solubility in SILMs is related to the IL molar volume.[39] Accordingly, and despite the narrow molar volume range of the ILs used in this work, the highest CO_2 solubilities were obtained in the SILMs made of [Ch][Lev] and [Ch][Mal], which also have the highest molar volumes (Supplementary Information, Table S2).

Table 1| Gas solubilities (S) in the prepared cholinium-based SILMs calculated from gas permeability and diffusivity values.

SILM	S CO_2 [a]	S CH_4 [a]	S N_2 [a]
[Ch][Lev]	170 ± 2.2	0.84 ± 0.05	0.55 ± 0.01
[Ch][Lac]	92 ± 2.2	0.85 ± 0.06	0.39 ± 0.01
[Ch][Gly]	93 ± 2.0	0.88 ± 0.01	0.50 ± 0.03
[Ch][Mal]	142 ± 1.6	0.69 ± 0.11	0.55 ± 0.05

[a] Solubility x 10^6 (m^3 (STP) m^{-3} Pa^{-1})

Overall, all of the cholinium-based SILMs tested exhibited larger CO_2 solubility values than that of the prototypical ionic liquids commonly used to prepare SILMs, which are based on fluorinated or nitrile-containing anions.[14, 15, 19, 21, 40] The anion nature seems to have a stronger influence on the gas solubility than the cation.[41] This is in agreement with the finding that the CO_2 absorption capacity can be drastically enhanced by using ILs combining basic anions, such as acetate [42] or amino acids,[43] because the CO_2 solvation in those ILs occurs through chemisorption schemes.[44]

The ideal selectivity (or permselectivity) was obtained by dividing the permeabilities of two different pure gases. The obtained ideal CO_2/CH_4 and CO_2/N_2 permselectivities of the cholinium-based SILMs are shown in Figure 4. Because the CH_4 permeability is greater than that of N_2 along the cholinium-based SILMs (Figure 2), the CO_2/CH_4 permselectivity is always smaller than CO_2/N_2 permselectivity (Figure 4). The largest CO_2/CH_4 and CO_2/N_2 permselectivities were achieved for the [Ch][Gly]-based SILM. Remarkably, the CO_2/CH_4 permselectivity herein reported for the [Ch][Gly] represents the highest value reported so far for SILMs. Figure 4 also shows a comparison between the CO_2/CH_4 and CO_2/N_2 permselectivities obtained in this work with those of other SILMs taken from literature.[15, 19, 21, 37, 40] For example, CO_2/CH_4 and CO_2/N_2 permselectivity values of 21.7 and 46.2, respectively, were obtained in the [Ch][Lac]-based SILM, which are slightly higher than those of 17.6 and 43.4 found in the SILM made of [C_2mim][Lac] (Figure 4).[37]

Actually, in general, the CO_2/CH_4 permselectivity of cholinium-based SILMs not only exceed the performance of imidazolium-ILs, but also of those of phosphonium-ILs and other ammonium-ILs different form cholinium.[19, 21] In addition, the CO_2/N_2 permselectivity is on par or greater than that of other reported SILMs, including those made of ILs combining nitrile-containing anions of proven potential for CO_2 separation.[14, 15, 40] These results undoubtedly show that

the cholinium carboxylate ionic liquids are competitive to the use of hazard cations carrying similar basic anions.

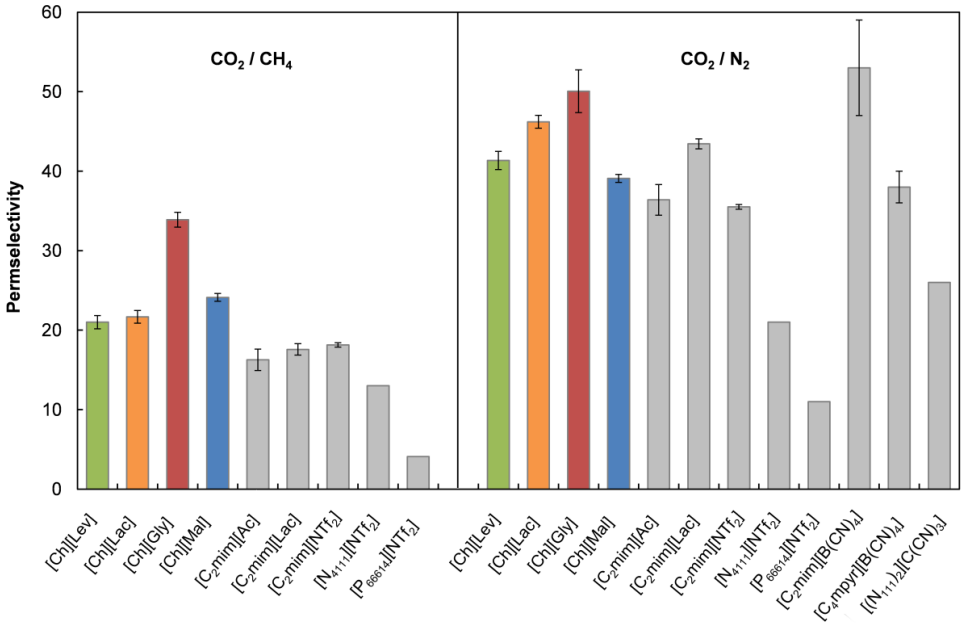

Figure 4| Permselectivity of CO_2/CH_4 and CO_2/N_2 in the cholinium-based SILMs. Literature data reported for other SILMs are also plotted for comparison.[15, 19, 21, 37, 40]

Although improved CO_2 permselectivities and high CO_2 solubilities were obtained, the permeability of cholinium-based SILMs toward dry gases was low compared to other families of ILs. The major bottleneck of using cholinium carboxylates in supported liquid membranes for gas separation processes is their high viscosities, which lead to long absorption equilibrium times. Thus, reducing the viscosity of cholinium carboxylates is certainly an important issue for their application as supported ionic liquid membranes. It is well reported that the viscosities of ILs drop when they absorb water.[45] Therefore, one possible way for increasing the gas permeability through these SILMs is to reduce the IL viscosity by the addition of water.

In conclusion, we have successfully prepared SILMs based on cholinium carboxylates which present both high CO_2 permselectivity and CO_2 solubility at 293 K under dry conditions. The results obtained in this work suggest that many opportunities exist for utilizing cholinium carboxylates in CO_2 separation applications. The high CO_2 permselectivities herein obtained together with the remarkable environmental-friendly properties and the simple and low production costs of cholinium carboxylates make these fluids a very attractive alternative for sustainable CO_2 separation processes.

3. Acknowledgements

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4. Supplementary Information

4.1. Materials

Cholinium bicarbonate solution (76 wt% in H_2O), levulinic acid (98%), malonic acid (99%), glycolic acid (99%) and diethyl ether (99.8 %) were purchased from Sigma-Aldrich. L-(+)-lactic acid solution (81 wt% in water) was supplied by Fluka.

Omnipore porous hydrophilic poly(tetrafluoroethylene) (PTFE) membranes provided by Merck Millipore, with a pore size of 0.2 μm and an average thickness of 65 μm, were used to support all the prepared cholinium-based ionic liquids. CO_2, N_2, and CH_4 were supplied by Air Liquide and were of at least 99.99% purity.

4.2. Methods and procedures

All the ILs were dried prior to use by stir-heating under vacuum (313-323 K, > 48 hours, ca. 10^{-3} kPa) and manipulated under inert atmosphere to prevent moisture absorption. Their water contents were determined by Karl Fischer titration (831 KF Coulometer, Metrohm).

Ionic liquids' purities were confirmed by ^{1}H- and ^{13}C-NMR spectroscopy (Bruker Avance 400 Ultrashield Plus), electrospray ionization mass spectrometry (LCQ 3-D iontrap MS Thermo Finnigan and Esquire 3000+ 3-D iontrap Bruker) and elemental analysis (Leco TruSpec® Series elemental analyser).

Ionic liquids' melting temperatures (T_m) were determined by differential scanning calorimetry (DSC, DSC Q200, TA Instrument). Samples (*ca.* 5 to 10 mg) were crimped in an aluminium standard pans and analysed under nitrogen atmosphere by heating (10 K min^{-1}) - cooling (5 K min^{-1}) cycles between 193.15 K and 353.15 K. T_m was determined as the local maximum of the endothermic peak on heating.

Measurements of viscosity and density were performed in the temperature range between 293.15 and 343.15 K at atmospheric pressure using an SVM 3000 Anton Paar rotational Stabinger viscometer-densimeter. The SVM 3000 uses Peltier elements for fast and efficient thermostability and the temperature uncertainty is ± 0.02 K. The precision of the dynamic viscosity measurements is ± 0.5 % and the absolute uncertainty of the density is ± 0.0005 g cm^{-3}. Triplicates of each IL sample were performed to ensure accuracy and the reported results are the average values with a maximum relative standard deviation (RSD) of 1.08%.

Gas permeabilities and diffusivities through the prepared cholinium carboxylate-based SILMs were measured using a time-lag apparatus (Figure S1). Details on the construction and operation of this experimental setup are entirely described elsewhere.[17] In the present work, all of the SILMs were degassed under vacuum inside the permeation cell during 24 hours before testing. The experimental gas measurements were conducted at 293 K for single gas feed with an upstream pressure of 100 kPa and vacuum (< 0.1 kPa) as the initial downstream pressure. At least three separate experiments of each gas on a single SILM sample were performed. Between experiments, the membrane sample was degassed under vacuum until the downstream pressure was below 0.1 kPa. No residual IL was found inside the permeation cell at the end of the experiments. The thickness of the SILM was assumed to be equivalent to the membrane filter thickness.

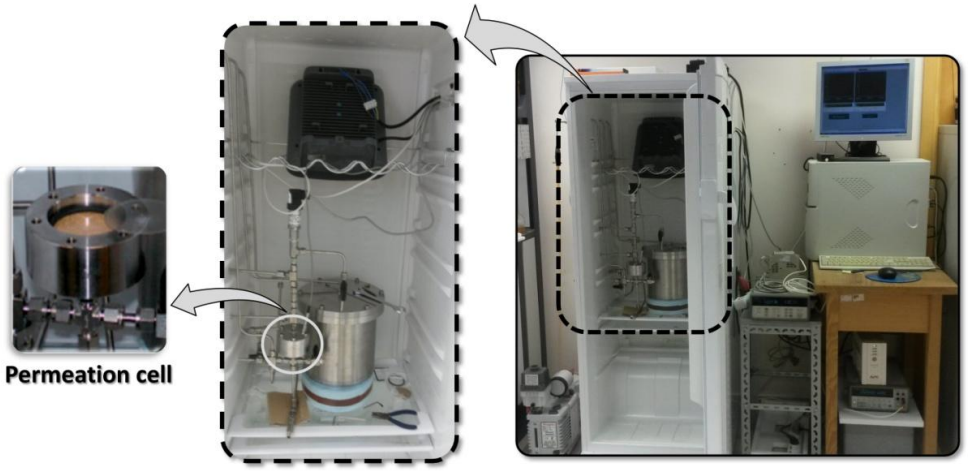

Figure S1| Time-lag apparatus and the stainless steel flat-type permeation cell used in this work.

4.3. Structural characterization

Cholinium L(+)lactate: ^{1}H-NMR (400 MHz, D_2O): δ_H/ppm = 1.32 (3 H, d, *J* 6.9 Hz, OOCCH(C**H**$_3$)OH); 3.20 (9 H, s, N(C**H**$_3$)$_3$); 3.51 (2 H, m, NC**H**$_2$CH$_2$OH); 4.06 (2 H, m, NCH$_2$C**H**$_2$OH); 4.11 (1 H, q, *J* 6.9 Hz, OOCC**H**(CH$_3$)OH). ^{13}C-NMR (101 MHz, D_2O):

δ_C/ppm = 20.00 (1C, OOCCH(**C**H_3)OH); 53.82 (3C, N(**C**H_3)$_3$); 55.55 (1C, NCH_2**C**H_2OH); 67.37 (1C, N**C**H_2CH_2OH); 68.36 (1C, OOC**C**H(CH_3)OH); 182.24 (1C, OO**C**CH(CH_3)OH). Elemental analysis (mass %) – Found: N, 7.07; C, 49.69; H, 9.71. Calculated for $C_8H_{19}NO_4$: N, 7.25; C, 49.72; H, 9.91. MS ES+ *m/z* (% rel. Intensity): 104 M^+ (100). Calc. for $C_5H_{14}NO$ 104.11, found 104.1. MS ES- *m/z* (% rel. Intensity): 89 M^- (100). Calculated for $C_3H_5O_3$ 89.02, found 89.0.

Cholinium levulinate: ^{1}H-NMR (400 MHz, D_2O): δ_H/ppm = 2.22 (3 H, s, OOCCH_2CH_2C(O)C**H**$_3$); 2.41 (2 H, t, *J* 6.8 Hz, OOCC**H**$_2$CH_2C(O)CH_3); 2.78 (2 H, t, *J* 6.8 Hz, OOCCH_2C**H**$_2$C(O)CH_3); 3.20 (9 H, s, N(C**H**$_3$)$_3$); 3.51 (2 H, m, NC**H**$_2$CH_2OH); 4.06 (2 H, m, NCH_2C**H**$_2$OH).^{13}C-NMR (101 MHz, D_2O): δ_C/ppm = 29.15 (1C, OOCCH_2CH_2C(O)**C**H$_3$); 31.07 (1C, OOC**C**H_2CH_2C(O)CH_3); 39.38 (1C, OOCCH_2**C**H_2C(O)CH_3); 53.82 (3C, N(**C**H_3)$_3$); 55.56 (1C, NCH_2**C**H_2OH); 67.38 (1C, N**C**H_2CH_2OH); 181.23 (1C, OO**C**CH_2CH_2C(O)CH_3); 215.03 (1C, OOCCH_2CH_2**C**(O)CH_3). Elemental analysis (mass %) – Found: N, 5.95; C, 54.80; H, 9.24. Calculated for $C_{10}H_{21}NO_4$: N, 6.39; C, 54.77; H, 9.65. MS ES+ *m/z* (% rel. Intensity): 104 M^+ (100). Calculated for $C_5H_{14}NO$ 104.11, found 104.1. MS ES- *m/z* (% rel. Intensity): 115 M^- (100). Calculated for $C_5H_7O_3$ 115.04, found 115.0.

Cholinium glycolate: ^{1}H-NMR (400 MHz, D_2O): δ_H/ppm = 3.20 (9 H, s, N(C**H**$_3$)$_3$); 3.51 (2 H, m, NC**H**$_2$CH_2OH); 3.94 (2 H, s, OOCC**H**$_2$OH); 4.06 (2 H, m, NCH_2C**H**$_2$OH). ^{13}C-NMR (101 MHz, D_2O): δ_C/ppm = 53.82 (3 C, N(**C**H_3)$_3$); 55.56 (1 C, NCH_2**C**H_2OH); 61.11 (1 C, OOC**C**H_2OH); 67.39 (1 C, N**C**H_2CH_2OH); 179.66 (1 C, OO**C**CH_2OH). Elemental analysis (mass %) – Found: N, 7.29; C, 46.50; H, 9.69. Calculated for $C_7H_{17}NO_4$: N, 7.82; C, 46.91; H, 9.56. MS ES+ *m/z* (% rel. Intensity): 104 M^+ (100). Calculated for $C_5H_{14}NO$ 104.11, found 104.5. MS ES- *m/z* (% rel. Intensity): 75 M^- (100). Calculated for $C_2H_3O_3$ 75.01, found 74.9.

Cholinium malonate: ^{1}H-NMR (400 MHz, DMSO-d_6): δ_H/ppm = 2.71 (2 H, s, OOCC**H**$_2$COOH); 3.11 (9 H, s, N(C**H**$_3$)$_3$); 3.40 (2 H, m, NC**H**$_2$CH$_2$OH); 3.83 (2 H, m, NCH$_2$C**H**$_2$OH). ^{13}C-NMR (101 MHz, DMSO-d_6): δ_C/ppm = 38.90 (1C, OOC**C**H$_2$COOH); 53.16 (3C, N(**C**H$_3$)$_3$); 55.14 (1C, NCH$_2$**C**H$_2$OH); 66.99 (1C, N**C**H$_2$CH$_2$OH); 171.70 (2C, OO**C**CH$_2$**C**OOH). Elemental analysis (mass %) – Found: N, 6.78; C, 46.58; H, 8.17. Calculated for $C_{10}H_{21}NO_4$: N, 6.76; C, 46.37; H, 8.27. MS ES+ *m/z* (% rel. Intensity): 104 M^+ (100). Calculated for $C_5H_{14}NO$ 104.11, found 104.1. MS ES- *m/z* (% rel. Intensity): 103 M^- (100). Calculated for $C_3H_3O_4$ 103.00, found 103.0.

4.4. Thermal properties

Melting temperatures (T_m) of the ILs prepared in this work and their water contents measured immediately previous to the DSC measurements are presented in Table S1.

Table S1| Melting temperature (T_m) of the cholinium-based ILs and their water contents prior to the DSC analyses.

Ionic liquid	wt% of water	T_m (K)
[Ch][Lac]	0.172	n.d.[a]
[Ch][Lev]	0.226	n.d.[a]
[Ch][Gly]	0.113	321.8[b]
[Ch][Mal]	0.097	n.d.[a]

[a] n.d. – no melting or crystallization peaks observed, *i.e*. samples are liquid between 193.15 and 353.15 K.

[b] The melting temperature values obtained for [Ch][Gly] is similar to that reported by Ohno *et al.*[2]

4.4. Density and viscosity

Density and viscosity of the prepared cholinium-ILs are summarized in Table S2. Additionally, density and viscosity results as a function of temperature are

illustrated in Figure S2 and Figure S3, respectively. The water contents measured prior the density and viscosity measurements were as follows: 0.38 wt% in [Ch][Lac], 0.57 wt% in [Ch][Lev], 0.44 wt% in [Ch][Gly] and 0.76 wt% in [Ch][Mal].

As it can be seen in Table S2, the density values of the cholinium-ILs studied vary between 1.092 and 1.178 g cm^{-3} at 343.15 K and from 1.122 to 1.208 g cm^{-3} at 293.15 K. The density values decrease linearly with the temperature for the four ILs studied. Moreover, [Ch][Lev] shows the lowest density values, while [Ch][Mal] display the higher, being the four ILs ordered as: [Ch][Lev]< [Ch][Lac]< [Ch][Gly]< [Ch][Mal]. It is know that the increase of the alkyl chain on the imidazolium cation leads to a decrease in density.[45] Muhammad *et al*.[46] have also observed an analogue behavior for [Ch][Propanoate], [Ch][Butanoate] and [Ch][Hexanoate]. On the other hand, the addition of one hydroxyl group or carboxylic group in the anion structure leads to an increase in the resulting density.[47]

The viscosity measurements presented in Table S2 and illustrated in Figure S3 show that, at 293.15 K, [Ch][Mal] (11883.7 mPa s) is three times more viscous than the other three ILs, which present viscosities ranging from 2426.8 to 3661.3 mPa s. The cholinium-ILs can be ordered by increasing viscosity as follows: [Ch][Lev] < [Ch][Gly] < [Ch][Lac] < [Ch][Mal]. At 343.15 K, the values are between 329.0 and 110.1 mPa s for [Ch][Mal] and [Ch][Lev], respectively, while [Ch][Lac] and [Ch][Gly] viscosities just differ less than 2%. In fact, their viscosities are quite similar over the entire range of temperatures most probably due to their similar chemical structures.

The molar volumes (V_m) of the cholinium-based ILs studied in this work were calculated from the density results and are presented in Table S3.

Table S2| Experimental viscosities (η) and densities (ρ) of the cholinium-based ionic liquids studied as a function of temperature.

	[Ch][Lac]		[Ch][Lev]		[Ch][Gly]		[Ch][Mal]	
T (K)	η (mPa s)	ρ (g cm^{-3})	η (mPa s)	ρ (g cm^{-3})	η (mPa s)	ρ (g cm^{-3})	η (mPa s)	ρ (g cm^{-3})
343.15	128.663	1.110	110.067	1.092	130.473	1.161	328.950	1.178
338.15	163.093	1.113	137.283	1.095	164.740	1.164	432.383	1.181
333.15	210.227	1.116	173.803	1.098	211.213	1.167	569.550	1.184
328.15	275.920	1.119	223.657	1.100	275.447	1.170	769.307	1.187
323.15	369.400	1.122	293.043	1.103	365.953	1.173	1053.967	1.190
318.15	505.443	1.125	391.597	1.106	496.313	1.176	1479.300	1.193
313.15	708.400	1.129	534.810	1.109	688.370	1.179	2126.600	1.197
308.15	1019.367	1.132	748.107	1.112	978.483	1.182	3136.700	1.200
303.15	1510.067	1.135	1074.500	1.116	1428.833	1.186	4758.267	1.203
298.15	2310.06	1.138	1588.933	1.119	2149.300	1.189	7425.967	1.206
293.15	3661.333	1.141	2426.767	1.122	3340.033	1.192	11883.667	1.208

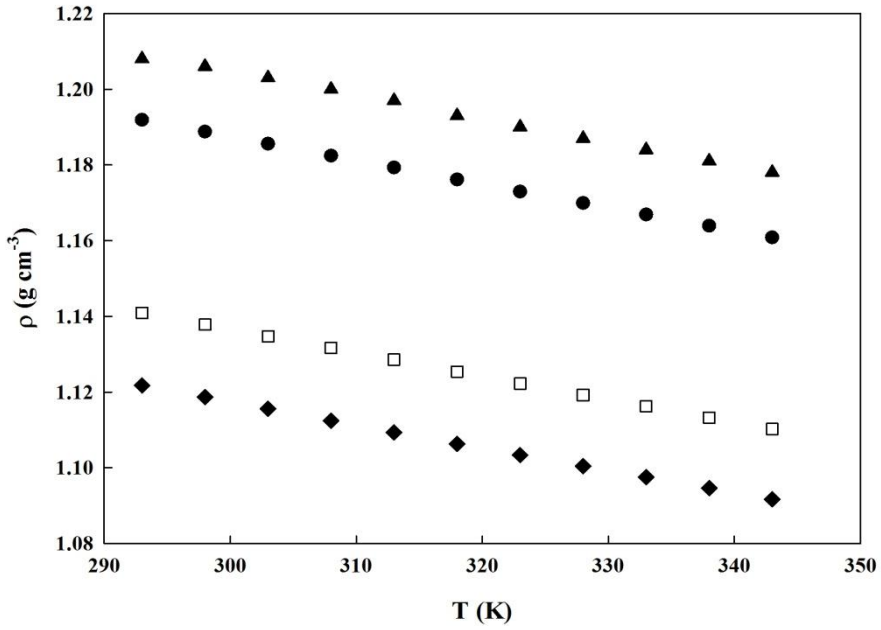

Figure S2| Experimental densities of the ionic liquids studied as a function of temperature: [Ch][Lac] (□), [Ch][Lev] (♦), [Ch][Gly] (●), [Ch][Mal] (▲).

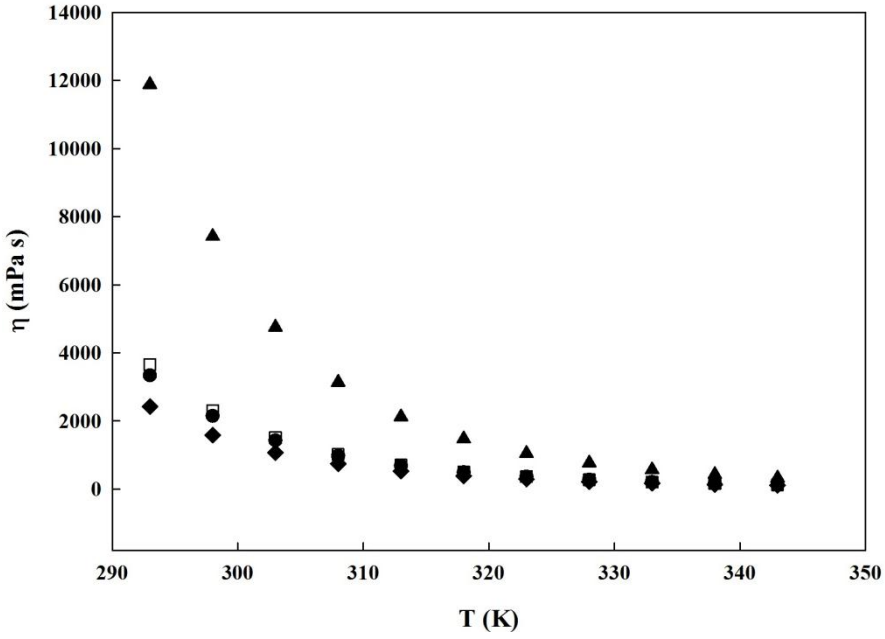

Figure S3| Experimental viscosities of the ionic liquids studied as a function of temperature: [Ch][Lac] (□), [Ch][Lev] (♦), [Ch][Gly] (●), [Ch][Mal] (▲).

Table S3 Calculated molar volumes, V_m ($cm^3\,mol^{-1}$), of the cholinium-based ionic liquids.

T (*K*)	[Ch][Lac]	[Ch][Lev]	[Ch][Gly]	[Ch][Mal]
343.15	174.06	200.86	154.39	175.98
338.15	173.59	200.32	153.98	175.52
333.15	173.12	199.79	153.59	175.04
328.15	172.66	199.27	153.19	174.57
323.15	172.20	198.74	152.80	174.10
318.15	171.72	198.20	152.39	173.65
313.15	171.23	197.67	151.97	173.19
308.15	170.76	197.12	151.57	172.75
303.15	170.30	196.56	151.17	172.31
298.15	169.84	196.02	150.76	171.90
293.15	169.38	195.47	150.36	171.53

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Chapter 3

Playing with ionic liquid mixtures to design engineered membranes for CO_2 separation

Part I: Mixing anions with different chemical natures

Part II: Mixing sulfate and cyano-functionalized anions

Chapter 3

Part I: Mixing anions with different chemical natures

Adapted from: **L.C. Tomé,** D.J.S. Patinha, C.S.R. Freire, L.P.N. Rebelo, I.M. Marrucho, CO_2 separation applying ionic liquid mixtures: the effect of mixing different anions on gas permeation through supported ionic liquid membranes, *RSC Adv.*, 2013, **3**, 12220 – 12229.

The author contributed to the planning and execution of all the experiments described in this chapter, except the density and viscosity measurements which were carried out by D.J.S. Patinha. The author was also involved on the discussion and interpretation of results, as well as, on the preparation of the manuscript.

1. Abstract

In order to increase the flexibility in tailoring the permeability and selectivity of supported ionic liquid membranes (SILMs) for flue gas separation and natural gas purification, this work explores the use of ionic liquid (IL) mixtures. For that purpose, gas permeation properties of CO_2, CH_4, and N_2 in several binary IL mixtures based on the 1-ethyl-3-methylimidazolium cation ($[C_2mim]^+$) and different anions such as bis(trifluoromethylsulfonyl)imide ($[NTf_2]^-$), acetate ($[Ac]^-$), lactate ($[Lac]^-$), dicyanamide ($[N(CN)_2]^-$) and thiocyanate ($[SCN]^-$) were measured. In addition to gas permeation results, the thermophysical properties of those mixtures, namely viscosity and density, were also determined so that trends between the two types of properties can be evaluated. The results show that mixing $[Ac]^-$ or $[Lac]^-$ with $[NTf_2]^-$ promotes the decrease of gas permeability and diffusivity of the SILMs based on those binary mixtures essentially due to their high viscosities. The pure ILs containing anions with nitrile groups, $[N(CN)_2]^-$ or $[SCN]^-$, and also their mixtures with $[C_2mim][NTf_2]$ exhibit permselectivities ranging from 19.1 to 23.0 for CO_2/CH_4, and from 36.6 to 67.8 for CO_2/N_2 permselectivities, as a consequence of a reduction in the CH_4 and N_2 permeabilities, respectively. Furthermore, it is shown that mixing anions with different chemical features allows variations in IL viscosity and mole volume that impact the gas permeation properties of SILMs offering a clear pathway for the optimization of their CO_2 separation performances.

2. Introduction

The topic of global warming, largely associated to the rising concentration of anthropogenic CO_2, is arguably one of the most important environmental issues that our world faces today. CO_2 emissions have been increasing and currently the power sector is the main responsible of the CO_2 emissions, which are related to

fuel combustion for generating energy or heat. The escalating level of atmospheric CO_2 and the urgency to take action for preventing irreversible climate change have hugely increased the efforts on the development of new efficient and economic technologies for carbon capture and storage.[1]

The most relevant current technologies used for the elimination of CO_2 from natural gas streams and power plants include absorption with amines, adsorption with porous solids, membrane and cryogenic separation,[2, 3] where amine-based absorption is undoubtedly the most common and efficient technology. Even though its advantages such as high reactivity and good absorption capacity, the use of amines involve several concerns related to their corrosive nature, volatility and high energy demand for regeneration.[4] Alternatively, membrane separation exhibits inherent advantages including small scale of the equipment, relative environmentally safety, ease of incorporation into existing processes, low energy consumption and operating costs.[5]

Despite the large array of polymeric membranes for CO_2 separation developed during the last decades,[6] there are still drawbacks to be overcome. That is the case of the low CO_2 permeability and selectivity of solid membranes. To circumvent this problem, supported liquid membranes have also been approached due to the high diffusion of gases in liquids when compared to solid membranes, leading to higher gas permeabilities.[7] Traditionally, in a supported liquid membrane, the selected solvent is immobilized into the pores of a solid membrane by capillary forces. Unfortunately, the long-term stability of the membrane can be affected by solvent depletion through the evaporation at specific operating conditions such as high temperature and pressure differentials. In order to overcome this drawback, the most interesting strategy is the use of ILs. Supported ionic liquid membranes have been studied owing to the intrinsic properties of ILs such as negligible volatility,[8] high thermal stability,[9] and low flammability,[10] making them ideal liquid phases for supported liquid membrane

applications. SILMs not only guarantee minimal membrane liquid loss through solvent evaporation but also allow more stable membranes due to the higher viscosity of ILs and greater capillary forces between the desired ionic liquid and the support membrane.[11, 12]

There has been a growing interest on the use of ILs in supported liquid membranes, particularly for CO_2 separations, not only due to the high levels of solubility and selectivity of CO_2 in these fluids relative to the other gases, namely CH_4 and N_2,[13-16] but also because of the ability to tailor many of their physical and chemical properties by combining different cations and anions or by adding functional groups.[17, 18] Consequently, several studies on the permeation properties of gases through SILM systems have explored the effect of the IL structure. Relating to the influence of the cation, a number of groups have investigated the gas permeation properties of different families of ILs (imidazolium,[19-30] phosphonium,[31, 32] sulphonium,[32] pyridinium,[33] and ammonium[34]) and improved results were obtained for imidazolium-based SILMs in terms of permeability and selectivity. Other studies, also focused on imidazolium ILs, explored different structural variations of the cation in order to enhance CO_2 solubility and selectivity.[35-37] On the other hand, the performance of imidazolium-based ILs containing several different anions has also been evaluated. Anions such as bis(trifluoromethylsulfonyl)imide ($[NTf_2]^-$),[19, 24, 27, 29] hexafluorophosphate ($[PF_6]^-$),[27, 38] trifluoromethanesulfonate ($[CF_3SO_3]^-$),[19, 24] dicyanamide ($[N(CN)_2]^-$),[19, 24, 39] tricyanomethane ($[C(CN)_3]^-$),[29, 39] tetracyanoborate ($[B(CN)_4]^-$),[39, 40] among others, have been tested and the results indicate that nitrile-containing anions promote an increase in both CO_2 permeability and CO_2/N_2 selectivity when compared to the $[NTf_2]^-$. In sum, it is important to emphasize that the ability to tailor the CO_2 affinity for the ionic liquid by combining different cations and anions is perhaps the most important feature of ILs for gas separation applications.

Recently, IL mixtures have been proposed as a mean to further increase flexibility and the fine-tune capacity of the physical and chemical properties of these remarkable compounds, providing an extra degree of freedom for the design of new solvents.[41, 42] However, only few works have explored the gas solubilities in binary IL + IL mixtures. Finotello *et al.* [43] measured the CO_2, CH_4 and N_2 solubilities of $[C_2mim][NTf_2]$ and $[C_2mim][BF_4]$ mixtures and the results showed that this approach can be used to enhance CO_2 solubility selectivity due to the control over IL molar volume. Shiflett and Yokozeki demonstrated that an IL mixture containing equimolar amounts of $[C_2mim][TFA]$ and $[C_2mim][Ac]$ has a combination of both chemical and physical absorption effects.[44] Wang *et al.* showed that improvements in CO_2 absorption performance can be obtained by mixing a functional IL $[NH_2C_2mim][BF_4]$ with low viscosity ILs, namely $[C_2mim][BF_4]$ and $[C_4mim][BF_4]$.[45] Although the use of IL mixtures seems to be a promising strategy, CO_2 separation using SILMs has never been attempted before.

Furthermore, a quick search in the literature on the subject of CO_2 solubility in ionic liquids shows a marked contrast either in terms of the number of publications or on the chemical diversity of the ILs researched. From amine inspired reactive ILs to aprotic heterocyclic anion ILs,[46] the most recent studies focus on task specific ILs by using basic anions, such as acetate,[47] aminoacids,[48] imidazolide or pyrrolide.[49]

In this work, the CO_2, CH_4, and N_2 permeation properties of IL mixtures through SILMs is researched. Taking into account that the anions of ILs have a stronger influence on CO_2 solubility than the cations [15, 50] and that the CO_2 molecules have a larger affinity for anion *versus* cation associations,[16, 51] this study examines IL + IL mixture systems with a common cation and different anions. Four ILs based on the $[C_2mim]^+$ cation combined with anions that have different CO_2 solubility behaviors (chemical solubility: $[Ac]^-$ and $[Lac]^-$; physical solubility: $[N(CN)_2]^-$ and $[SCN]^-$) were mixed with $[NTf_2]^-$. The chemical structures of the ILs

used in this study are presented in Figure 1. In order to explore the CO_2 separation performance trends of IL mixtures, supported ionic liquid membranes with different proportions of each anion were prepared. Since generally permeability in SILMs scales with viscosity while selectivity scales with mole volume, the thermophysical properties, namely density and viscosity, of the prepared IL + IL mixtures were also measured and discussed.

3. Experimental Section

3.1. Materials

IoLiTec GmbH provided the 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_2mim][NTf_2]$) (99 wt% pure), 1-ethyl-3-methylimidazolium dicyanamide ($[C_2mim][N(CN)_2]$) (> 98 wt% pure), and 1-ethyl-3-methylimidazolium acetate ($[C_2mim][Ac]$) (> 95 wt% pure). Aldrich supplied the 1-ethyl-3-methylimidazolium L-(+)-lactate ($[C_2mim][Lac]$) (≥ 95 wt% pure). The 1-ethyl-3-methylimidazolium thiocyanate ($[C_2mim][SCN]$) (≥ 95 wt% pure) was purchased from Fluka.

To reduce the content of water and other volatile substances, all the pure IL samples were dried under vacuum (10^{-3} kPa) and subject to vigorous stirring at a moderated temperature (≈ 318 K) for at least 4 days immediately prior to use. The water contents of the pure ILs, determined by Karl Fischer titration (831 KF Coulometer, Metrohm), are presented in Table 1. The larger water contents of both $[C_2mim][Ac]$ and $[C_2mim][Lac]$ are most probably due to the hydrophilic nature of their anions. No further purification of the ILs was carried out, but their purities were confirmed by ^1H RMN analysis.

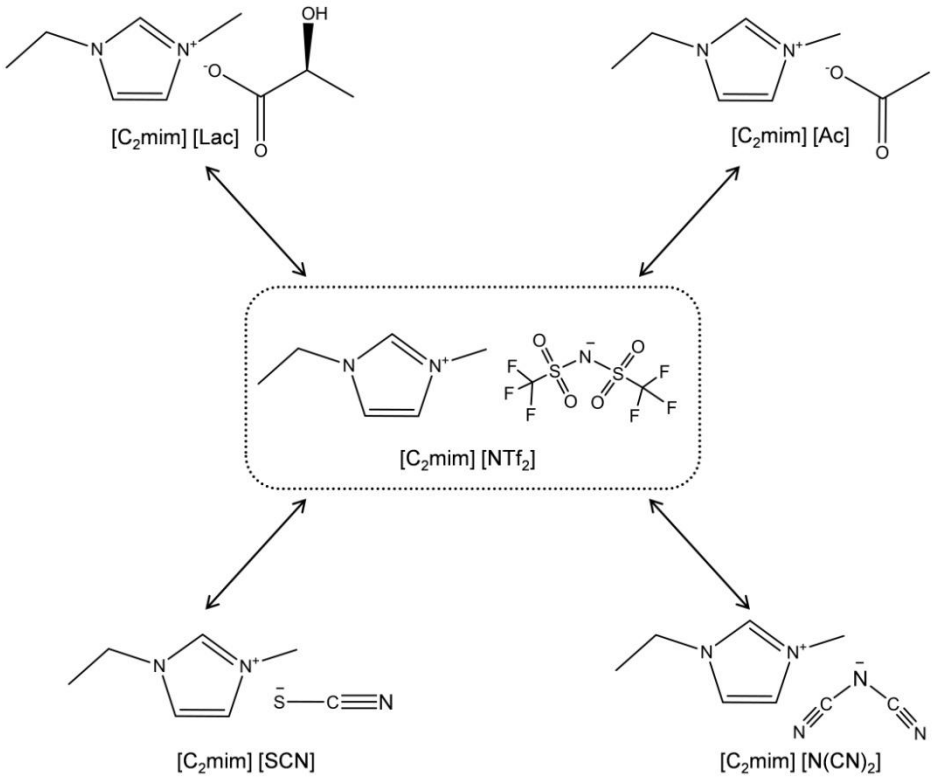

Figure 1| Chemical structures and short names of the ionic liquids used in this work.

3.2. Preparation of the ionic liquid mixtures

The binary mixtures of IL + IL with different mole fractions were prepared using an analytical high-precision balance with an uncertainty of ± 10^{-5} g by syringing known masses of the IL components into glass vials. Good mixing was assured by magnetic stirring for at least 30 minutes. Then, the prepared IL mixtures were dried under vacuum (10^{-3} kPa) at a moderate temperature (≈ 318 K) for another 4 days. The samples were prepared immediately prior to the measurements to avoid variations in composition. The composition descriptions of the prepared IL + IL mixtures as well as their water contents determined by Karl Fischer titration are presented in Table 1.

3.3. Viscosity and density determination

Measurements of viscosity and density for the pure ILs and their mixtures were performed in the temperature range between 293.15 and 343.15 K at atmospheric pressure using an SVM 3000 Anton Paar rotational Stabinger viscometer-densimeter. This equipment uses Peltier elements for fast and efficient thermostability. The temperature uncertainty is ± 0.02 K. The precision of the dynamic viscosity measurements is ± 0.5% and the absolute uncertainty of the density is ± 0.0005 g cm^{-3}. The overall uncertainty of the viscosity measurements (taking into account the purity and handling of the samples) was estimated to be 2%.[52] Further details on the equipment can be found elsewhere.[53] At least 3 measurements of each sample were performed to ensure accuracy and the reported results are the average value.

3.4. Preparation of supported ionic liquid membranes

Durapore porous hydrophobic poly(vinylidene fluoride) (PVDF) membrane, with a pore size of 0.22 µm, average thickness of 125 µm, acquired from Millipore Corporation (USA) was only used to support the pure $[C_2mim][NTf_2]$. PVDF membrane filters have extensively been used in other works for the same purpose.[24, 28, 32] What is more, Neves *et al.* demonstrated that the stability of the hydrophobic PVDF membrane is larger than that of the hydrophilic PVDF.[27] Even though these membrane filters are characterized by their chemical resistance, we found that the impregnation of $[C_2mim][N(CN)_2]$, $[C_2mim][Ac]$, $[C_2mim][Lac]$ or $[C_2mim][SCN]$ into the pores of hydrophobic PVDF resulted in unstable SILMs. In order to overcome this drawback and improving the chemical resistance and compatibility of the support, porous hydrophilic poly(tetrafluoroethylene) (PTFE) membranes provided by Merck Millipore, with a pore size of 0.2 µm and average thickness of 65 µm, were used to prepare all the SILMs which are made of ILs

containing the $[N(CN)_2]^-$, $[Ac]^-$, $[Lac]^-$ or $[SCN]^-$ anions.

To achieve stable SILMs, much care should be taken to ensure that the liquid sample completely fills the membranes pores. In this work, the SILM configuration process only used 1 mL of the pure ILs or their mixtures (previously dried). First, the membrane filter was introduced inside a vacuum chamber for 1 hour in order to remove the air within the pores and facilitate the membrane wetting. Then, drops of the IL sample were spread on the membrane surface using a syringe, while keeping the vacuum inside the chamber. As the liquid penetrated into the membrane pores, the membrane became transparent. The SILM was left inside the chamber under vacuum for another 1 hour. Finally, the SILM was taken out of the chamber and the excess of IL was wiped from the membrane surfaces with paper tissue. The amount of the sample immobilized was determined gravimetrically by weighing the membrane filter before and after impregnation. The membrane thickness was also confirmed using a digital micrometer (Mitutoyo, model MDE-25PJ, Japan).

3.5. Gas permeation measurements

Experimental measurements of CO_2, CH_4, and N_2 permeation through the prepared SILMs were conducted for single gas feed using a time-lag apparatus, which allows for the simultaneous determination of permeability and diffusivity. Details on the construction and operation of this experimental setup are entirely described elsewhere.[54] Briefly, this system consists of two chambers (feed and permeate) separated by the permeation cell. Each prepared SILM was positioned on the top of a highly porous sintered disk for providing mechanical stability and installed into the permeation cell where it was degassed under vacuum during 12 hours before testing. The gas permeation experiments were performed at 293 K with an upstream pressure of 100 kPa (feed) and vacuum (< 0.1 kPa) as the initial downstream pressure (permeate). All permeation values are the result of at least

three separate experiments of each gas on a single SILM sample. Between experiments, the permeation cell and lines were evacuated on both upstream and downstream sides until the pressure was below 0.1 kPa. No residual ionic liquid was found inside the permeation cell at the end of the experiments. The thickness of the SILM was assumed to be equivalent to the membrane filter thickness.

The gas transport through a liquid membrane occurs according a solution-diffusion mass transfer mechanism where the permeability (*P*) is related to solubility (*S*) and diffusivity (*D*) as follows:[55]

$$P = S \times D \tag{1}$$

Permeability (*P*) is defined as the steady-state gas flux (*J*) through a membrane under a transmembrane pressure drop (Δ*p*) and normalized to the unit thickness of the membrane as follows:[56]

$$P = J \frac{\ell}{\Delta p} \tag{2}$$

The flux was determined experimentally using Equation 3, where V^p is the permeate volume, Δp_d is the variation of downstream pressure, *A* is the effective membrane surface area, *t* is the experimental time, *R* is the Ideal Gas Law constant and *T* is the absolute temperature.

$$J = \frac{V^p \Delta p_d}{AtRT} \tag{3}$$

Diffusivity (*D*) was obtained according to Equation 4. The time-lag parameter (θ), which can be obtained before achieving steady-state flux, was deduced by extrapolating the slope of the linear portion of the p_d vs. *t* curve back to the time axis, where the intercept is equal to θ.[57]

$$D = \frac{\ell^2}{6\theta} \tag{4}$$

After knowing both *P* and *D*, it was also possible to calculate *S* using the relationship shown in Equation (1).

The ideal permeability selectivity (or permselectivity), $\alpha_{i/j}$, was obtained by dividing the permeability of the more permeable specie *i* to the permeability of the less permeable specie *j*. As shown in Equation (5), the permselectivity can also be expressed as the product of the diffusivity selectivity and the solubility selectivity.

$$\alpha_{i/j} = \frac{P_i}{P_j} = \left(\frac{D_i}{D_j}\right) \times \left(\frac{S_i}{S_j}\right) \quad (5)$$

4. Results and Discussion

The structures of the pure ILs used and the composition description of the prepared binary mixtures are shown in Figure 1 and Table 1, respectively. The viscosity and density of the pure ILs and the binary IL mixtures reported in Table 1 were measured in this work and a detail description of these data in a temperature range from 293.15 to 343.15 K is presented and discussed in Supplementary Information.

4.1. Gas permeability and permselectivity

To the best of our knowledge, this is the first report on gas permeation properties of binary IL + IL mixtures supported membranes. Permeability and ideal permselectivity values of the prepared SILMs towards the measured gases are summarized in Table 2.

Table 1| Composition descriptions and physical properties of the pure ionic liquids and their mixtures used to prepare the SILMs studied.

Ionic liquid sample	Composition (Mole fraction)	wt% of water	M (g mol^{-1})	η (mPa s)[a]	ρ (g cm^{-3})[a]	V_m (cm^3 mol^{-1})[b]
$[C_2mim][NTf_2]$	pure	0.02	391.31	39.085	1.524	256.78
$[C_2mim][NTf_2]_{0.75}[Ac]_{0.25}$	x $[C_2mim][NTf_2]$ = 0.75 + x $[C_2mim][Ac]$ = 0.25	0.08	336.04	60.936	1.451	231.55
$[C_2mim][NTf_2]_{0.5}[Ac]_{0.5}$	x $[C_2mim][NTf_2]$ = 0.5 + x $[C_2mim][Ac]$ = 0.5	0.14	280.76	98.011	1.362	206.17
$[C_2mim][NTf_2]_{0.25}[Ac]_{0.75}$	x $[C_2mim][NTf_2]$ = 0.25 + x $[C_2mim][Ac]$ = 0.75	0.48	225.49	127.927	1.249	180.53
$[C_2mim][Ac]$	Pure	0.49	170.21	164.930	1.101	154.61
$[C_2mim]$ $[NTf_2]_{0.5}[Lac]_{0.5}$	x $[C_2mim][NTf_2]$ = 0.5 + x $[C_2mim][Lac]$ = 0.5	0.37	295.77	103.633	1.365	216.64
$[C_2mim][Lac]$	Pure	0.54	200.23	370.413	1.145	174.87
$[C_2mim][NTf_2]_{0.5}[N(CN)_2]_{0.5}$	x $[C_2mim][NTf_2]$ = 0.5 + x $[C_2mim][N(CN)_2]$ = 0.5	0.12	284.26	29.169	1.362	208.66
$[C_2mim][N(CN)_2]$	Pure	0.09	177.21	17.947	1.106	160.24
$[C_2mim][NTf_2]_{0.5}[SCN]_{0.5}$	x $[C_2mim][NTf_2]$ = 0.5 + x $[C_2mim][SCN]$ = 0.5	0.04	280.28	38.600	1.371	204.39
$[C_2mim][SCN]$	Pure	0.09	169.25	27.846	1.119	151.24

[a] Viscosity (η) and density (ρ) measured at 293.15 K.

[b] Molar volume (V_m) obtained for 293.15 K.

Table 2| Gas permeabilities (*P*) and ideal permselectivities (*α*) obtained in the prepared SILMs.[a]

SILM sample	Gas Permeability (Barrer)[b]				
	P CO_2	*P* CH_4	*P* N_2	α CO_2/CH_4	α CO_2/N_2
$[C_2mim][NTf_2]$	589 ± 1.0	32.5 ± 0.42	16.6 ± 0.11	18.1 ± 0.3	35.5 ± 0.3
$[C_2mim][NTf_2]_{0.75}[Ac]_{0.25}$	503 ± 1.8	28.3 ± 0.41	15.7 ± 0.28	17.8 ± 0.2	33.4 ± 0.7
$[C_2mim][NTf_2]_{0.5}[Ac]_{0.5}$	336 ± 3.4	18.9 ± 0.04	10.0 ± 0.10	17.7 ± 0.2	33.4 ± 0.7
$[C_2mim][NTf_2]_{0.25}[Ac]_{0.75}$	214 ± 0.4	12.6 ± 0.06	6.20 ± 0.19	17.0 ± 0.1	34.4 ± 1.1
$[C_2mim][Ac]$	118 ± 5.8	7.26 ± 0.24	3.25 ± 0.01	16.3 ± 1.3	36.4 ± 1.9
$[C_2mim]$ $[NTf_2]_{0.5}[Lac]_{0.5}$	265 ± 0.4	14.6 ± 0.19	7.20 ± 0.05	18.2 ± 0.3	36.8 ± 0.3
$[C_2mim][Lac]$	55 ± 0.3	3.13 ± 0.11	1.27 ± 0.01	17.6 ± 0.7	43.4 ± 0.6
$[C_2mim][NTf_2]_{0.5}[N(CN)_2]_{0.5}$	589 ± 1.9	30.9 ± 0.29	14.1 ± 0.18	19.1 ± 0.2	41.8 ± 0.7
$[C_2mim][N(CN)_2]$	476 ± 0.8	20.7 ± 0.01	7.03 ± 0.05	23.0 ± 0.1	67.8 ± 0.6
$[C_2mim][NTf_2]_{0.5}[SCN]_{0.5}$	516 ± 0.2	25.7 ± 0.07	14.1 ± 0.07	20.1 ± 0.1	36.6 ± 0.2
$[C_2mim][SCN]$	263 ± 0.6	12.1 ± 0.06	4.65 ± 0.15	21.8 ± 0.2	56.6 ± 1.9

[a] The listed uncertainties represent the standard deviations, based on three experiments.
[b] Barrer (1 Barrer = 10^{-10} cm^3(STP)cm cm^{-2} s^{-1} $cmHg^{-1}$)

A comparison of CO_2 permeability and CO_2/N_2 and CO_2/CH_4 permselectivities determined in this work with the values reported by Scovazzo *et al.* for $[C_2mim][N(CN)_2]$[19] and by Bara *et al.* for $[C_2mim][NTf_2]$[36] is shown in Table 3. These works were selected for comparison since the same experimental technique was used. The differences between CO_2 permeability and ideal permselectivities can be explained by the different measurement conditions, namely temperature and trans-membrane pressure differential, as well as, the different supports used (Table 3). Close *et al.*[30] have recently shown that the gas permeability through a SILM is influenced by the support membrane due to the difference between the IL interactions and the solid interfaces. Additionally, the presence of impurities or water in the IL greatly affect their physical[58, 59] and gas permeation properties.[26] Since both Scovazzo *et al.*[19] and Bara *et al* [36] did not report this information, an

exact comparison cannot be made. These differences in results highlight the importance of measuring the properties of the pure ILs so that trends can be clearly established and comparisons between SILMs with pure ILs and their binary mixtures confidently performed.

Table 3| Comparison of CO_2 permeability and ideal CO_2/N_2 and CO_2/CH_4 permselectivity values measured in this work to values reported in literature.

	This work	Other works
$[C_2mim][NTf_2]$		Bara *et al.* [36]
Membrane support	PVDF	PES
Measurement conditions	293 K, 100 kPa	296 K, 85 kPa
P CO_2 (Barrer)	589	680
α CO_2/N_2	35.5	31
α CO_2/CH_4	18.1	14
η (mPa s)	39.085	N/A
Water content (wt%)	0.02	N/A
Purity (wt%)	99	N/A
$[C_2mim][N(CN)_2]$		Scovazzo *et al.*[19]
Membrane support	PTFE	PES
Measurement conditions	293 K, 100 kPa	303 K, 20 kPa
P CO_2 (Barrer)	476	610
α CO_2/N_2	68	61
α CO_2/CH_4	23	20
η (mPa s)	17.947	21
Water content (wt%)	0.09	N/A
Purity (wt%)	98	N/A

Table 2 shows that the same trend of permeability values was observed for all the SILMs tested: P CO_2 > P CH_4 > P N_2 and, accordingly, α CO_2/N_2 is always greater than α CO_2/CH_4. In fact, the CO_2 permeability is always one or two orders of magnitude higher than that of CH_4 and N_2. Although the highest gas

permeabilities were obtained for the $[C_2mim][NTf_2]$-based SILM, the largest CO_2/CH_4 and CO_2/N_2 permselectivities of 23.0 and 67.8, respectively, were achieved for $[C_2mim][N(CN)_2]$. Actually, the CO_2 permeability of $[C_2mim][N(CN)_2]$ decreases 24%, while the CH_4 and N_2 permeabilities decrease 57 and 136%, respectively, compared to $[C_2mim][NTf_2]$ (Table 2). Thus, the highest permselectivities of $[C_2mim][N(CN)_2]$ are essentially due to the more pronounced decrease of CH_4 and N_2 permeabilities than that of CO_2. In addition, a similar result was also observed for the SILM made of pure $[C_2mim][SCN]$ due to identical decreases in the gas permeability values. This result demonstrates that the SILMs based on $[SCN]^-$ anions, whose experimental gas permeation properties are here reported for the first time, are capable of achieving high CO_2/N_2 permselectivities (Table 2). These findings are in line with other recently published studies, where ILs with other nitrile-containing anions lead to higher ideal CO_2/N_2 permselectivities compared to the $[NTf_2]^-$.[29, 39, 40]

Regarding the IL mixtures, mixing $[C_2mim][Ac]$ or $[C_2mim][Lac]$ with $[C_2mim][NTf_2]$ has a significant influence in the gas permeability properties of the SILMs. For instance, 0.5 mole fraction of $[C_2mim][Ac]$ in $[C_2mim][NTf_2]$ decreases CO_2, CH_4 and N_2 permeabilities by 75%, 72% and 66%, respectively while, for the 0.5 mole fraction of $[C_2mim][Lac]$, permeability decays of 122%, 123% and 130% occurred. In contrast, 0.5 mole fraction of $[C_2mim][SCN]$ just decreases 14%, 26% and 18% the CO_2, CH_4 and N_2 permeabilities, respectively. Moreover, 0.5 mole fraction of $[C_2mim][N(CN)_2]$ did not affect the CO_2 permeability and hardly affects the CH_4 and N_2 permeabilities compared to those of the pure $[C_2mim][NTf_2]$-based SILM.

The comparison of CO_2/CH_4 and CO_2/N_2 separation efficiencies between the results obtained in this work and the available data for SILMs is plotted in Figure 2 in the form of Robeson plots.[6] These plots, which are commonly used to evaluate the performance of membrane materials given a particular gas separation,

demonstrate the compromise that exists between both the high selectivity and permeability. Since the upper bound of a Robeson plot is based on large amounts of experimental data for each separation,[6] data points above this line can be considered as an improvement over the current membrane state of the art.

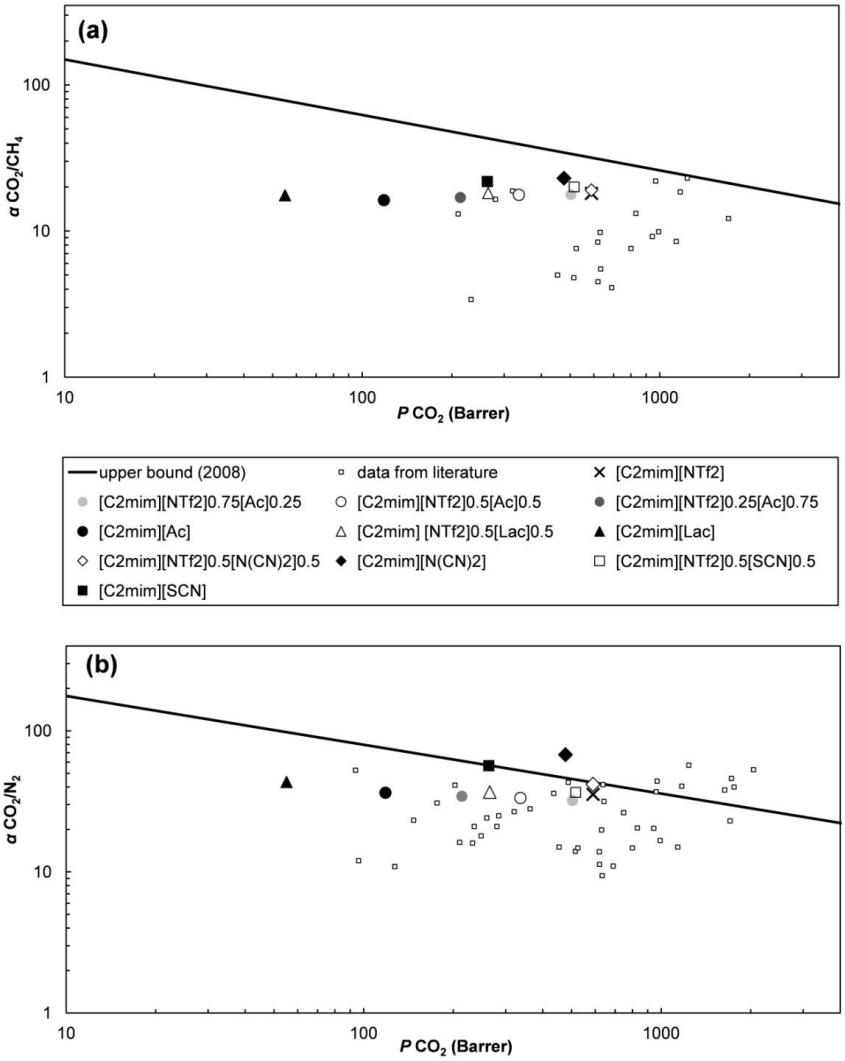

Figure 2| Robeson plots of the studied gases in the prepared SILMs. Data are plotted on a log-log scale and the upper bound for each gas pair is adapted from Robeson.[6] (a) CO_2/CH_4 permselectivity versus CO_2 permeability and (b) CO_2/CH_4 permselectivity *versus* CO_2 permeability. Literature data reported for other supported ionic liquid membranes are also plotted in (a)[24, 31, 34, 36] and (b).[24, 29, 31, 32, 34, 36, 40, 60, 61]

Figure 2(a) shows that the results obtained in this work for CO_2/CH_4 separation are bellow the upper bound, close to those available in literature for other pure ILs. However, SILMs made of pure $[C_2mim][Ac]$ and $[C_2mim][Lac]$ are exceptions since their CO_2/CH_4 separation performances fall in a empty data region of this plot, with much lower permeabilities than those obtained for other supported ionic liquid membranes. Regarding CO_2/N_2 separation, the SILM prepared with $[C_2mim][N(CN)_2]$ is above the upper bound, while the SILMs of the binary mixture $[C_2mim][NTf_2]_{0.5}[N(CN)_2]_{0.5}$ and the pure $[C_2mim][SCN]$ are on top of the line (Figure 2(b)). Furthermore, Figure 2 clearly shows that the CO_2 separation performance of SILMs as a function of the permeability can be fine-tune by mixing different anions. For instance, mixtures of $[Ac]^-$ or $[Lac]^-$ with the $[NTf_2]^-$ anion causes a dramatic shift of the results along the *x*-axis without significantly sacrificing of the CO_2/CH_4 and CO_2/N_2 permselectivities. Thus, our results demonstrate that is possible to adjust and design the SILMs permeability just by mixing anions which have different chemical natures and physical properties.

4.2. Gas diffusivity

Gas diffusivity is a mass transfer property that affects gas permeability through SILMs as described by Equation (1). The higher the diffusivity, the faster the gas passes through the SILM. In general, ionic liquids that have larger viscosity will form SILMs with smaller permeability.[62] The experimental gas diffusivities obtained in this work at 293 K are plotted in Figure 3.

The measured CO_2 diffusivity in $[C_2mim][NTf_2]$-based SILM is on the order of 10^{-10} m^2 s^{-1}, which is consistent with the values reported by other research groups.[21, 63] From Figure 3 it can be seen that the SILMs with lower gas diffusivities are $[C_2mim][Ac]$ and $[C_2mim][Lac]$, which also have the lowest gas permeabilities (Table 2) and the highest viscosities (Table 1). On the other hand, $[C_2mim][N(CN)_2]$

has the lowest viscosity but the highest gas permeabilities belong to $[C_2mim][NTf_2]$-based SILM. This means that not only the diffusivity plays an important role on gas permeability of the SILM but the solubility should also be considered.

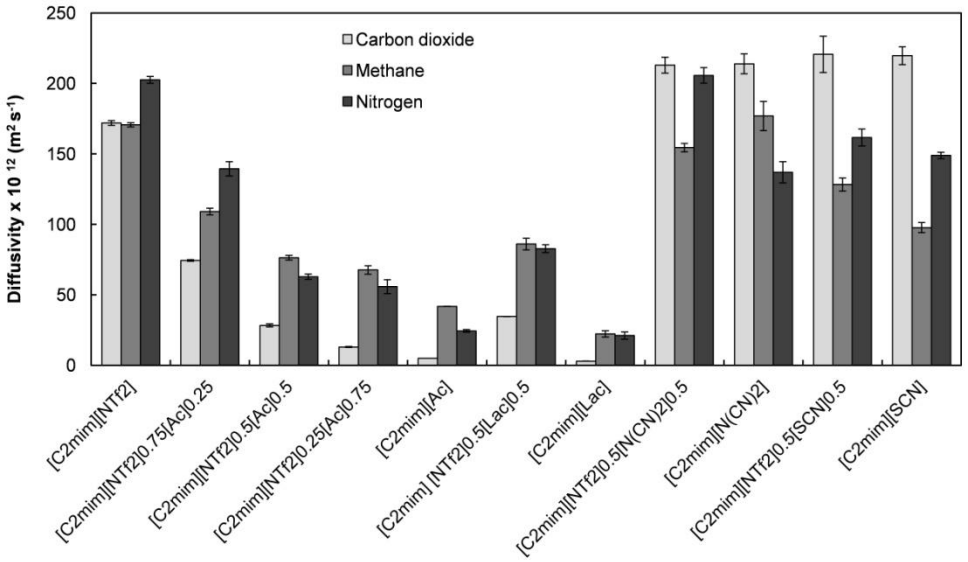

Figure 3| Gas diffusivity through the prepared SILMs. Error bars represent standard deviations based on three experimental replicas.

Scovazzo[21, 31, 34] and Baltus[33, 63] have already showed that gas diffusivities in ILs are one or more orders of magnitude slower than in traditional solvents, essentially due to higher viscosities of ILs. Additionally, they also found that literature correlations for gas diffusivity in conventional solvents are inadequate to describe the gas diffusivity in ILs.[21, 63] In view of that, several different correlations for gas diffusivity in different IL families have been developed considering the effect of temperature, solute mole volume, solvent viscosity, solvent density and solvent molecular weight.[21, 31, 33, 34, 63]

In Figure 4(a) the relationship between gas diffusivity and IL viscosity, for the $[C_2mim][NTf_2][Ac]$ binary mixtures is shown. A wide range of viscosities was

obtained for these mixtures, from 30 up to 170 mPa s. For the three studied gases, an increase in the mixture viscosity, due to the increment of $[C_2mim][Ac]$ mole fraction, corresponds to a decrease in the diffusivity. This behavior, also observed for the mixture of $[C_2mim][NTf_2]_{0.5}[Lac]_{0.5}$ (Figure 3 and Table 1), is similar to the previously proposed general trends observed for other pure SILMs.[21, 31, 34] In contrast, for the $[C_2mim][NTf_2]_{0.5}[SCN]_{0.5}$ and $[C_2mim][NTf_2]_{0.5}[N(CN)_2]_{0.5}$ mixtures different behaviors were found as shown in Figure 4(b). Although the differences in viscosities, the presence of 0.5 mole fraction of $[C_2mim][NTf_2]$ in those two mixtures did not significantly affect their CO_2 diffusivity, whereas different changes in CH_4 and N_2 diffusivities compared to the pure $[C_2mim][N(CN)_2]$ and $[C_2mim][SCN]$ were observed. Furthermore, the results obtained in this work for pure $[C_2mim][NTf_2]$, $[C_2mim][N(CN)_2]$ and $[C_2mim][SCN]$ SILMs surprisingly showed that CH_4 and N_2 diffusivity trends follow unexpected sequences, from the highest to the lowest value, $[N(CN)_2]^- \sim [NTf_2]^- > [SCN]^-$ and $[NTf_2]^- > [N(CN)_2]^- \sim [SCN]^-$, respectively, contrasting to their viscosity trend $[NTf_2]^- > [SCN]^- > [N(CN)_2]^-$. This is a clear evidence that the description of the gas diffusivity in terms of IL viscosity only does not provide a full understanding of the different behaviors obtained since it is possible to have, for the same gas, different diffusivities in SILMs (pure IL or mixtures) that have the same viscosity.

4.3. Gas solubility

The CO_2, CH_4 and N_2 solubilities obtained in this work using Equation (1) are shown in Figure 5. The same trend obtained for the permeability ($P\ CO_2 > P\ CH_4 > P\ N_2$) (Table 2), was also observed for the solubility of all the prepared SILMs: $S\ CO_2 > S\ CH_4 > S\ N_2$. From Figure 5, it can be observed that $[C_2mim][Ac]$ exhibits the highest CO_2 solubility followed by $[C_2mim][Lac]$, surpassing the $[C_2mim][NTf_2]$-based SILMs. The addition of 0.5 mole fraction of $[C_2mim][Ac]$ or $[C_2mim][Lac]$ to

$[C_2mim][NTf_2]$ increases 242% and 119% the CO_2 solubility, respectively, compared to the pure $[C_2mim][NTf_2]$. Conversely, 0.5 mole fraction of $[C_2mim][SCN]$ or $[C_2mim][N(CN)_2]$ promotes a CO_2 solubility decrease of 189% and 24%, respectively. It has been recognized that gas solubility in SILMs is related to IL molar volume.[64]

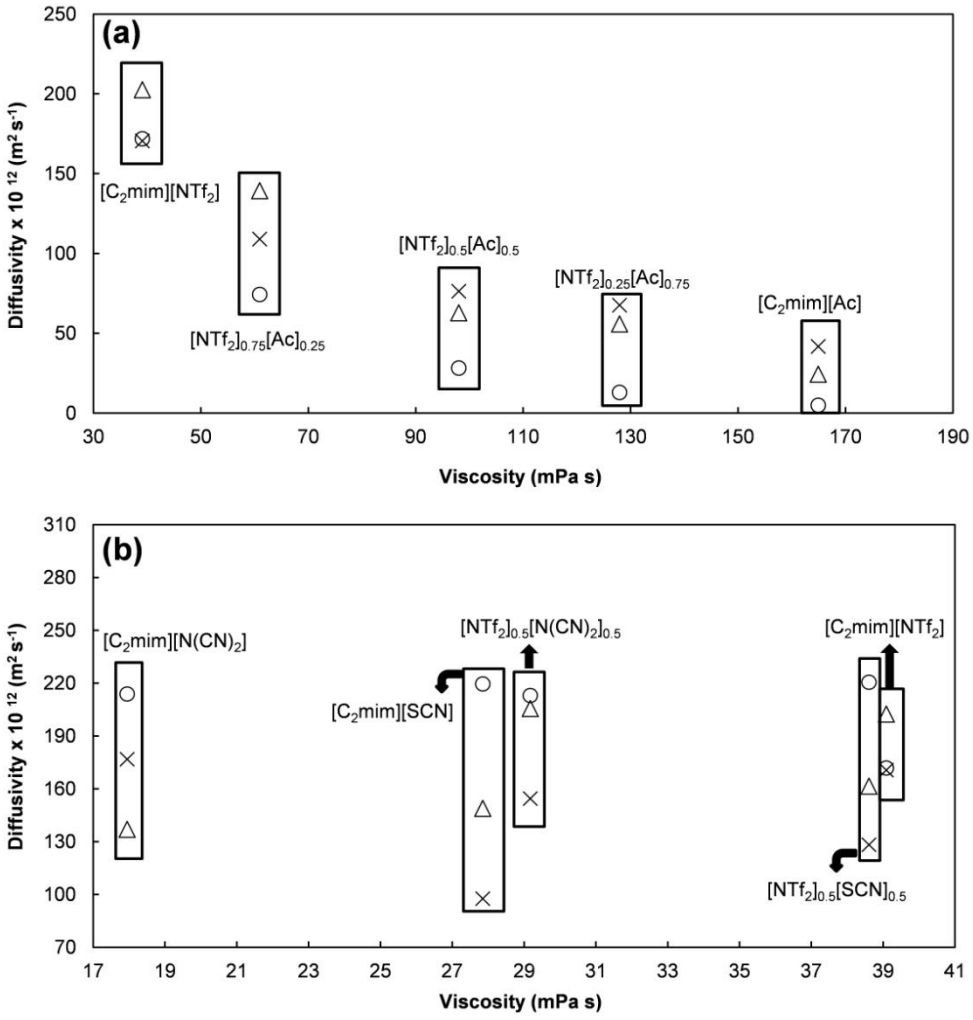

Figure 4| Carbon dioxide (○), methane (×) and nitrogen (△) diffusivities in SILMs as function of measured IL viscosity.

Two correlations for gas solubilities in ionic liquids based on the regular solution theory, with direct application to SILMs, have been proposed: Camper *et al*.[64] developed a model that uses only the molar volume of the IL to predict gas solubility and solubility selectivity, while Kilaru and Scovazzo proposed a two parameter model (the so-called Universal Model) that includes the IL molar volume and viscosity and covers an extended set of ionic liquid families.[65] The Camper Model was developed using only imidazolium-based ILs data with non-coordinating anions such as $[N(CN)_2]^-$, $[NTf_2]^-$, $[BF_4]^-$ or $[CF_3SO_3]^-$. According to this model, the solubility is given by:

$$S = \left\{ \left[\exp\left(\alpha + \frac{\beta}{(V_m)^{4/3}} \right) \right] V_m \right\}^{-1} \quad (6)$$

where α and β are gas specific parameters, S is the gas solubility (in moles of gas per liter of ionic liquid) and V_m is the IL molar volume. The solubility selectivity can be calculated by the ratio of Equation (6) solved for each gas in the gas pair. The result is a prediction of an exponential increase in solubility selectivity as the IL molar volume decreases.[64]

Figure 6 displays the solubility selectivity values of the SILMs studied in this work versus IL molar volume, as well as the Camper Model. As can be clearly seen in Figure 6(a) and Figure 6(b), the CO_2/CH_4 and CO_2/N_2 solubility selectivity trends of the pure $[C_2mim][NTf_2]$, $[C_2mim][N(CN)_2]$, $[C_2mim][SCN]$ and their respective binary mixtures are in reasonable agreement with the Camper Model. For example, mixtures of different ILs, such as $[C_2mim][NTf_2]_{0.5}[N(CN)_2]_{0.5}$ and $[C_2mim][NTf_2]_{0.5}[SCN]_{0.5,}$ with similar molar volumes, have roughly the same solubility selectivity which can be described by the Camper Model. Nevertheless, for $[C_2mim][Ac]$, $[C_2mim][Lac]$, and also for their binary mixtures with $[C_2mim][NTf_2]$, the Camper Model is not suitable to describe their CO_2/N_2 and CO_2/CH_4 solubility selectivities as shown in Figure 6. It is well documented that the

CO_2 solvation in [C_2mim][Ac] occurs through a chemical reaction scheme, still not fully understood, which is responsible for the high solubility.[66-68] This contrasts with the physical solubility scheme observed for the ILs used in the derivation of the Camper Model. This means that the Camper Model is not a general model for imidazolium-based ILs, as claimed by the authors but, in fact, limited by the anion nature of the ILs used in its derivation or in other words limited to ILs where CO_2 physical solubility occurs. Deviations to the Camper Model,[64] and also to the Universal Model,[65] were observed for the CO_2/CH_4 solubility selectivity in imidazolium-ILs combining alkylsulfate and alkylsulfonate anions.[69] The authors correlated these deviations with the low solubility of CH_4 in these ILs, which was explained using Kamlet-Taft β-parameter (the hydrogen bond donor capacity) that is governed by the anion basicity.

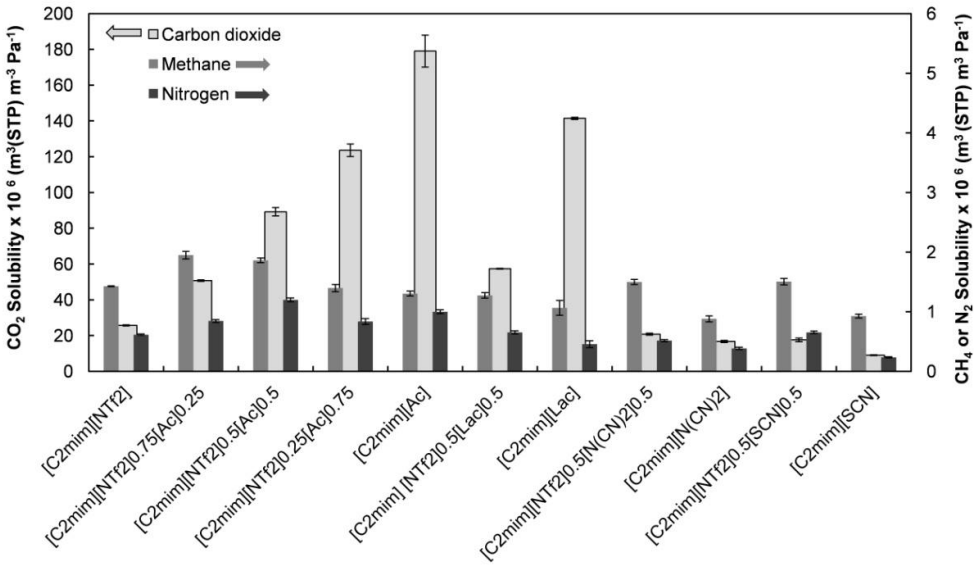

Figure 5| Gas solubility in the SILMs studied, calculated using Equation (1).

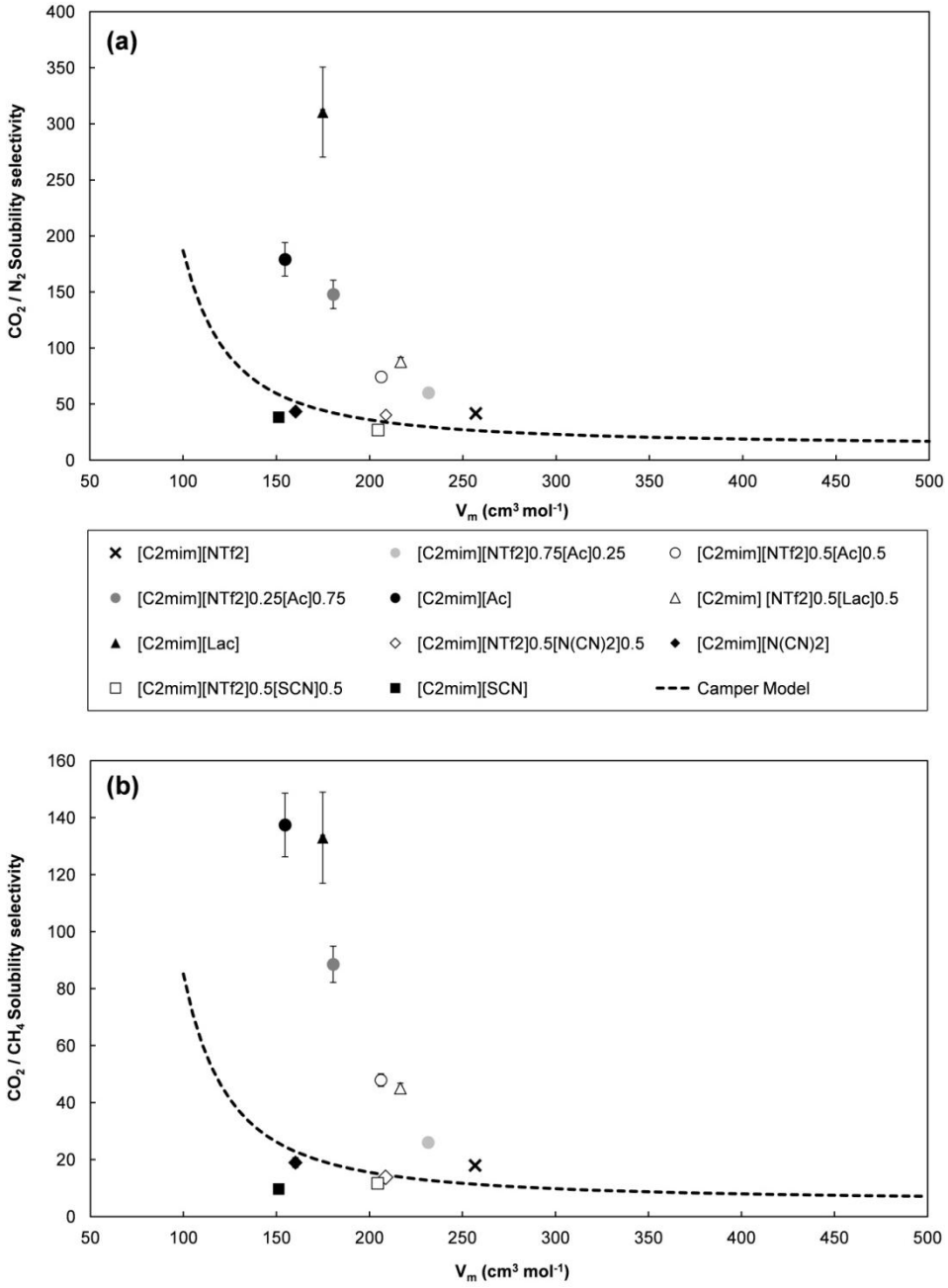

Figure 6| Solubility selectivity of the prepared SILMs plotted versus IL molar volume. For both figures (a) and (b), the error is either within the size of the markers or shown by error bars. The dashed lines represent the solubility selectivity predicted by the Camper Model for each gas pair.[64]

Interestingly, the solubility selectivity of CO_2 to CH_4 and N_2 in $[C_2mim][NTf_2]$-based SILMs can be enhanced by adding $[C_2mim][Ac]$ or $[C_2mim][Lac]$, as shown in Figure 6. The addition of 0.25, 0.5 and 0.75 mole fraction of $[C_2mim][Ac]$ promotes enhancements of 44%, 166% and 392% in the CO_2/CH_4 solubility selectivity, while for CO_2/N_2 increases of 44%, 78% and 254% were obtained. Moreover, 0.5 mole fraction of $[C_2mim][Lac]$ increases 150% the CO_2/CH_4 and 110% the CO_2/CH_4 solubility selectivity. Despite these CO_2 solubility selectivity enhancements in $[C_2mim][NTf_2]$ by mixing $[Ac]^-$ and $[Lac]^-$, the CO_2/N_2 and CO_2/CH_4 permselectivities did not drastically change (Table 2). This fact is essentially due to the decrease in diffusivity selectivity obtained for these IL mixtures, since for CO_2/N_2 diffusivity selectivity, values of 0.2 and 0.1 were obtained in the pure $[C_2mim][Ac]$ and $[C_2mim][Lac]$-based SILMs, respectively. Similarly, a CO_2/CH_4 diffusivity selectivity value of 0.1 was achieved for both SILMs. Given that, SILMs based on pure $[C_2mim][Ac]$ or $[C_2mim][Lac]$ and also their mixtures do not follow the usual behavior that permselectivity in SILMs is essentially dominated by solubility selectivity. Actually, diffusivity selectivity in a SILM is expected to be proportional to the ratio of gas molar volumes (approximately one) as generally observed for SILMs performed with pure ILs.[62]

5. Conclusions

Permeability, diffusivity and solubility of CO_2, N_2, and CH_4 in different IL mixtures using supported liquid membrane configurations were measured. Results showed that IL mixtures is an easy and promising strategy to perform CO_2 separation using supported ionic liquid membranes, since the IL properties can be tuned by mixing anions with completely different chemical character.

The CO_2/CH_4 separation performance of all the SILMs prepared in this work is similar to that of SILMs containing only pure ILs. Regarding CO_2/N_2 separation performance, the pure $[C_2mim][N(CN)_2]$ clearly exceed the Robeson upper bound

and both the $[C_2mim][NTf_2]_{0.5}[N(CN)_2]_{0.5}$ mixture and the pure $[C_2mim][SCN]$-based SILMs are on the upper bound, which makes them promising candidates for CO_2/N_2 separation applications.

The Camper Model provides a good description of the CO_2/CH_4 and CO_2/N_2 solubility selectivity values for the $[C_2mim][NTf_2][N(CN)_2]$ or $[C_2mim][NTf_2][SCN]$ mixtures. However, this model fails in describing the solubility selectivity of the $[C_2mim][NTf_2][Ac]$ or $[C_2mim][NTf_2][Lac]$ binary mixtures.

Even though higher CO_2 solubility selectivity improvements were obtained by mixing $[NTf_2]^-$ with $[Ac]^-$ or $[Lac]^-$, the CO_2/N_2 and CO_2/CH_4 permselectivities of those binary mixtures did not significantly change due to a significant decreased in the diffusivity selectivities. Nonlinear trends were found relating gas permeability and diffusivity with the viscosity, but the overall results showed that mixing ILs that have higher viscosities with $[NTf_2]^-$ decreases the gas permeability and diffusivity of the mixtures. In addition, the highest CO_2 separation performances were found for the less viscous mixtures of ILs, meaning that a proper balance combining both the most selective and the less viscous anions is crucial to achieve improved CO_2 separation performances.

6. Acknowledgements

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7. Supplementary Information

7.1. Density

Density of the pure ionic liquids (ILs) and their mixtures were measured in the temperature range from 293.15 to 343.15 K and are presented in Tables S1 and S2, and also illustrated in Figures S1 and S2, respectively. A comparison with literature is shown in Table S3 and the differences observed can be attributed to the low water content of our samples, since few authors do not report the water contents. The density values, ρ (g cm^{-3}), are fitted as a function of temperature, T (K), by the method of the least squares using the linear expression given by Equation (S1):

$$\rho = a + b\,(T) \tag{S1}$$

where a and b are adjustable parameters which are listed in Table S4ı. Moreover, in Table S5 and Table S6 the molar volumes of the pure ILs and their mixtures, respectively, are presented. The excess molar volume (V^E) resulting from the IL mixtures was calculated by Equation (S2):

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho_M} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \tag{S2}$$

where ρ and x are densities and mole fractions from, respectively, the two pure IL, identified with subscript numbers and subscript M refers to the IL mixture. The calculated excess molar volumes values are listed in Table S7 and depicted in Figure S3 at 293 K.

As it can be seen in Figure S1 and Figure S2, the density values of mixtures are in between those of the pure ILs, as expected. This fact is also confirmed for the $[C_2mim][NTf_2][Ac]$ mixture, where the density of the mixture $[C_2mim][NTf_2]_{0.5}[Ac]_{0.5}$ is in between the densities for the other two $[C_2mim][NTf_2][Ac]$ mixtures. It is interesting to see that there are some mixtures

with very distinct anions, such as $[C_2mim][NTf_2][SCN]$, $[C_2mim][NTf_2][N(CN)_2]$ and $[C_2mim][NTf_2][Ac]$, that have similar density values. Regarding the volume changes of a mixture, those can be the result of chemical, physical and structural modifications.[70] Physical contributions cause positive V^E values resulting from non-specific interactions between the real species present in the mixture.[71] The chemical interactions that include charge-transfer type forces, changes in hydrogen bonding equilibrium or electrostatic interactions, as well as the structural contributions that arise from geometrical fitting, contributes to negative V^E values.[72] All the studied mixtures show positive V^E, and therefore, the interactions between pure ILs molecules are stronger than those between different IL. This hinders the packing of the $[C_2mim][NTf_2]$ and thus increases the excess molar volume.

Table S1| Experimental densities (ρ) of the pure ionic liquids studied.

T (K)	ρ (g cm^{-3})				
	$[C_2mim][NTf_2]$	$[C_2mim][SCN]$	$[C_2mim][Lac]$	$[C_2mim][N(CN)_2]$	$[C_2mim][Ac]$
293.15	1.524	1.119	1.145	1.106	1.101
298.15	1.519	1.116	1.141	1.103	1.098
303.15	1.514	1.113	1.138	1.099	1.095
308.15	1.509	1.110	1.134	1.096	1.092
313.15	1.504	1.107	1.131	1.093	1.089
318.15	1.499	1.104	1.128	1.090	1.086
323.15	1.494	1.101	1.124	1.086	1.083
328.15	1.489	1.098	1.121	1.083	1.080
333.15	1.485	1.095	1.118	1.080	1.077
338.15	1.480	1.092	1.114	1.077	1.074
343.15	1.475	1.089	1.111	1.074	1.071

Table S2| Experimental densities (ρ) of the ionic liquids mixtures studied.

T (K)	ρ (g cm^{-3})					
	$[C_2mim][NTf_2]_{0.5}[SCN]_{0.5}$	$[C_2mim][NTf_2]_{0.5}[Lac]_{0.5}$	$[C_2mim][NTf_2]_{0.5}[N(CN)_2]_{0.5}$	$[C_2mim][NTf_2]_{0.5}[Ac]_{0.5}$	$[C_2mim][NTf_2]_{0.75}[Ac]_{0.25}$	$[C_2mim][NTf_2]_{0.25}[Ac]_{0.75}$
293.15	1.371	1.365	1.362	1.362	1.451	1.249
298.15	1.367	1.361	1.358	1.358	1.447	1.245
303.15	1.363	1.356	1.354	1.353	1.442	1.242
308.15	1.359	1.352	1.349	1.349	1.437	1.238
313.15	1.355	1.348	1.345	1.345	1.433	1.234
318.15	1.350	1.344	1.341	1.341	1.428	1.231
323.15	1.346	1.339	1.337	1.337	1.423	1.227
328.15	1.342	1.335	1.333	1.333	1.419	1.224
333.15	1.338	1.331	1.329	1.329	1.414	1.220
338.15	1.334	1.327	1.325	1.324	1.410	1.216
343.15	1.330	1.323	1.320	1.320	1.405	1.213

Table S3| Density (ρ) and viscosity (η) comparison with literature at 298K.

Ionic liquid sample	η (mPa s)		ρ (g cm^{-3})	
	This work	Literature	This work	Literature
$[C_2mim][NTf_2]$	32.4300	33.001 [73]	1.5190	1.51910 [74]
$[C_2mim][Lac]$	246.5070	169.000 [75]	1.1410	1.14606 [75]
$[C_2mim][Ac]$	119.2800	132.910 [76]	1.0979	1.09778 [76]
$[C_2mim][N(CN)_2]$	15.4260	14.900 [76]	1.1025	1.10198 [76]
$[C_2mim][SCN]$	23.4310	22.150 [77]	1.1160	1.1168 [78, 79]

Table S4| Fitted parameters of the linear expression given by Equation (S1).

Ionic liquid sample	$b \times 10^{-4}$	a	r^2
$[C_2mim][NTf_2]$	-9.78	1.5431	0.9999
$[C_2mim][SCN]$	-5.95	1.1308	0.9998
$[C_2mim][Lac]$	-6.76	1.1582	0.9998
$[C_2mim][N(CN)_2]$	-6.46	1.1186	0.9999
$[C_2mim][Ac]$	-5.98	1.1128	0.9999
$[C_2mim][NTf_2]_{0.5}[SCN]_{0.5}$	-8.23	1.3876	0.99994
$[C_2mim][NTf_2]_{0.5}[Lac]_{0.5}$	-8.48	1.3820	0.99991
$[C_2mim][NTf_2]_{0.5}[N(CN)_2]_{0.5}$	-8.38	1.3789	0.99994
$[C_2mim][NTf_2]_{0.5}[Ac]_{0.5}$	-8.27	1.3781	0.99994
$[C_2mim][NTf_2]_{0.75}[Ac]_{0.25}$	-9.16	1.4694	0.99992
$[C_2mim][NTf_2]_{0.25}[Ac]_{0.75}$	-7.23	1.2634	0.99996

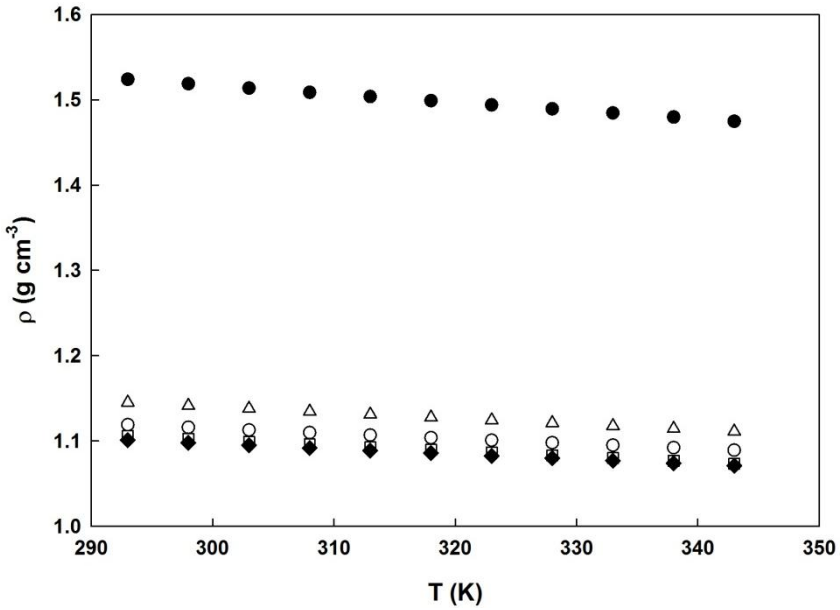

Figure S1| Experimental densities of the pure ionic liquids: $[C_2mim][NTf_2]$ (●), $[C_2mim][Ac]$ (♦), $[C_2mim][N(CN)_2]$ (□), $[C_2mim][Lac]$ (Δ), $[C_2mim][SCN]$ (○).

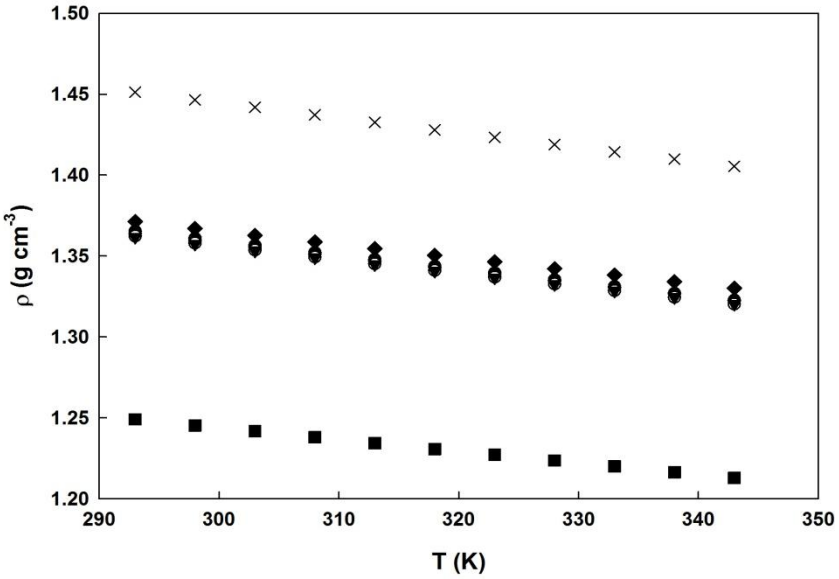

Figure S2| Experimental densities of the ionic liquid mixtures: $[C_2mim][NTf_2]_{0.5}[Lac]_{0.5}$ (●), $[C_2mim][NTf_2]_{0.5}[Ac]_{0.5}$ (▼), $[C_2mim][NTf_2]_{0.75}[Ac]_{0.25}$ (x), $[C_2mim][NTf_2]_{0.25}[Ac]_{0.75}$ (■), $[C_2mim][NTf_2]_{0.5}[N(CN)_2]_{0.5}$ (○), $[C_2mim][NTf_2]_{0.5}[SCN]_{0.5}$ (♦).

Table S5| Calculated molar volumes, V_m ($cm^3\ mol^{-1}$), of the pure ionic liquids studied.

T (K)	$[C_2mim][NTf_2]$	$[C_2mim][SCN]$	$[C_2mim][N(CN)_2]$	$[C_2mim][Lac]$	$[C_2mim][Ac]$
293.15	256.78	151.24	160.24	174.87	154.61
298.15	257.64	151.66	160.73	175.42	155.04
303.15	258.51	152.08	161.22	175.96	155.47
308.15	259.36	152.50	161.70	176.51	155.90
313.15	260.21	152.91	162.19	177.02	156.34
318.15	261.06	153.33	162.65	177.56	156.77
323.15	261.92	153.74	163.13	178.08	157.19
328.15	262.73	154.15	163.61	178.61	157.62
333.15	263.59	154.55	164.10	179.14	158.05
338.15	264.44	154.96	164.59	179.67	158.49
343.15	265.34	155.38	165.08	180.21	158.93

Table S6| Calculated molar volumes, V_m ($cm^3\ mol^{-1}$), of the ionic liquid mixtures studied.

T (K)	$[C_2mim][NTf_2]_{0.5}[SCN]_{0.5}$	$[C_2mim][NTf_2]_{0.5}[Lac]_{0.5}$	$[C_2mim][NTf_2]_{0.5}[N(CN)_2]_{0.5}$	$[C_2mim][NTf_2]_{0.5}[Ac]_{0.5}$	$[C_2mim][NTf_2]_{0.75}[Ac]_{0.25}$	$[C_2mim][NTf_2]_{0.25}[Ac]_{0.75}$
293.15	204.39	216.64	208.66	206.17	231.55	180.53
298.15	205.03	217.34	209.32	206.82	232.30	181.06
303.15	205.66	218.04	209.99	207.46	233.06	181.59
308.15	206.29	218.74	210.66	208.11	233.81	182.13
313.15	206.91	219.44	211.31	208.75	234.57	182.68
318.15	207.55	220.13	211.96	209.40	235.32	183.21
323.15	208.18	220.81	212.63	210.04	236.08	183.75
328.15	208.82	221.51	213.30	210.68	236.83	184.28
333.15	209.45	222.20	213.95	211.33	237.59	184.82
338.15	210.07	222.90	214.62	211.98	238.35	185.37
343.15	210.73	223.61	215.30	212.64	239.09	185.92

Table S7| Calculated excess molar volumes, V^E ($cm^3\ mol^{-1}$), of the ionic liquid mixtures.

T (K)	$[C_2mim][NTf_2]_{0.5}[SCN]_{0.5}$	$[C_2mim][NTf_2]_{0.5}[Lac]_{0.5}$	$[C_2mim][NTf_2]_{0.5}[N(CN)_2]_{0.5}$	$[C_2mim][NTf_2]_{0.5}[Ac]_{0.5}$	$[C_2mim][NTf_2]_{0.75}[Ac]_{0.25}$	$[C_2mim][NTf_2]_{0.25}[Ac]_{0.75}$
293.15	0.3730	0.8192	0.1506	0.4800	0.3136	0.3782
298.15	0.3797	0.8102	0.1331	0.4756	0.3113	0.3751
303.15	0.3636	0.8061	0.1227	0.4738	0.3047	0.3658
308.15	0.3610	0.8079	0.1236	0.4810	0.3140	0.3633
313.15	0.3510	0.8174	0.1117	0.4780	0.3235	0.3708
318.15	0.3541	0.8250	0.1046	0.4831	0.3375	0.3700
323.15	0.3486	0.8129	0.1028	0.4902	0.3442	0.3749
328.15	0.3821	0.8353	0.1245	0.5074	0.3762	0.3852
333.15	0.3739	0.8344	0.1097	0.5100	0.3808	0.3880
338.15	0.3706	0.8465	0.1021	0.5119	0.3897	0.3858
343.15	0.3665	0.8365	0.0912	0.5048	0.3578	0.3863

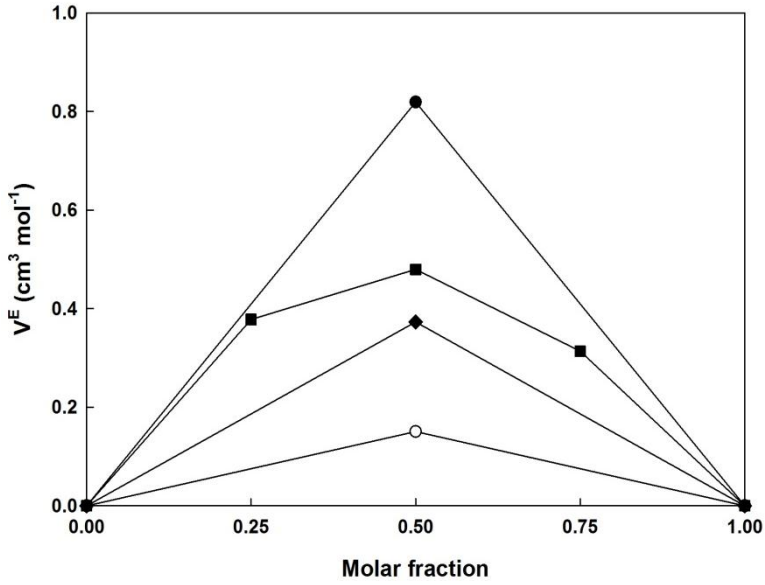

Figure S3| Excess molar volumes of the ionic liquid mixtures at 293.15 K: [C_2mim][NTf_2][Lac] (●), [C_2mim][NTf_2][Ac] (■), [C_2mim][NTf_2][$N(CN)_2$] (○), [C_2mim][NTf_2][SCN] (◆).

7.2. Viscosity

Viscosities of the pure ILs and their mixtures from 293.15 to 343.15 K are reported in Table S8 and Table S9 as well as represented in Figure S4 and Figure S5, respectively. The viscosity deviations ($\Delta\eta$) resulting from the IL mixtures were calculated by Equation (S3):

$$\Delta \ln(\eta) = \ln(\eta_M) - [x_1 \ln(\eta_1) + (1 - x_1) \ln(\eta_2)] \quad \text{(S3)}$$

where η and x are respectively, viscosities and mole fractions from the two pure ILs identified with subscript numbers. Subscript M refers to the IL mixture. The calculated values are presented in Table S10. The viscosity deviations calculated at 293 K are represented in Figure S6. Dynamic viscosities were fitted as a function of temperature, using an Arrehnius-like law:

$$\ln(\eta) = \ln(a) - \frac{E_a}{RT} \quad \text{(S4)}$$

where E_a is the activation energy, R is the gas constant, T is the temperature in Kelvin, a is the pre-exponential factor and η is the viscosity in mPa s. The fitted parameters are listed in Table S11❙ .

Taking into account Table S8 and Table S9, the viscosity trend is similar to that of the density. The viscosity values of the IL mixtures tend to be between those of the two pure ILs. Concerning the viscosity deviations, negative values are usually obtained for systems where molecular size and shapes of the components dispersion and dipolar interactions are considered,[58] whereas charge transfer and hydrogen bonding interactions lead to positive Δln*(η)* values.[58, 72] In the mixtures studied, only [C_2mim][Lac] shows negative deviation maybe due to the asymmetry and different size of the lactate anion when compared to the other anions, that are linear like thiocyanate or dicyanamide, or have minor sizes, such as the acetate anion. Nevertheless, the deviations from ideality are very small. In terms of activation energies, as it can be seen in Table S11❙ , the pure [C_2mim][Lac] shows the higher E_a (45 kJ mol^{-1}), followed by [C_2mim][Ac] (37 kJ mol^{-1}). Higher activation energies are related to the lower mobility of the ions, due to strong molecular interactions or entanglement of chains. The activation energies of the pure fluids can be ranked in the following order [C_2mim][$N(CN)_2$] < [C_2mim][SCN] < [C_2mim][NTf_2] < [C_2mim][Ac] < [C_2mim][Lac]. The same order is also observed for the mixtures of these ILs with [C_2mim][NTf_2] and the activation energies have values between those of the pure fluids. The overall viscosities together with activation energies can be increasingly aligned as: [C_2mim][$N(CN)_2$] < [C_2mim][SCN] < [C_2mim][NTf_2]$_{0.5}$[$N(CN)_2$]$_{0.5}$ < [C_2mim][NTf_2] < [C_2mim][NTf_2]$_{0.5}$[SCN]$_{0.5}$ < [C_2mim][NTf_2]$_{0.75}$[Ac]$_{0.25}$ < [C_2mim][NTf_2]$_{0.5}$[Ac]$_{0.5}$ < [C_2mim][NTf_2]$_{0.5}$[Lac]$_{0.5}$ < [C_2mim][NTf_2]$_{0.25}$[Ac]$_{0.75}$ < [C_2mim][Ac] < [C_2mim][Lac].

Table S8| Experimental viscosities (η) of the pure ionic liquids studied as a function of temperature at atmospheric pressure.

	η (mPa s)				
T (K)	$[C_2mim][NTf_2]$	$[C_2mim][SCN]$	$[C_2mim][Lac]$	$[C_2mim][N(CN)_2]$	$[C_2mim][Ac]$
293.15	39.085	27.846	370.413	17.947	164.930
298.15	32.430	23.431	246.507	15.426	119.280
303.15	27.157	19.937	170.927	13.366	88.883
308.15	23.126	17.146	122.763	11.696	67.973
313.15	19.911	14.900	90.967	10.323	53.129
318.15	17.301	13.058	69.270	9.177	42.369
323.15	15.164	11.538	54.006	8.222	34.377
328.15	13.403	10.269	42.983	7.410	28.328
333.15	11.920	9.200	34.842	6.712	23.670
338.15	10.721	8.289	28.699	6.115	20.017
343.15	9.655	7.511	23.973	5.597	17.116

Table S9| Experimental viscosities (η) of the ionic liquid mixtures studied as a function of temperature at atmospheric pressure.

T (K)	η (mPa s)					
	$[C_2mim][NTf_2]_{0.5}[SCN]_{0.5}$	$[C_2mim][NTf_2]_{0.5}[Lac]_{0.5}$	$[C_2mim][NTf_2]_{0.5}[N(CN)_2]_{0.5}$	$[C_2mim][NTf_2]_{0.5}[Ac]_{0.5}$	$[C_2mim][NTf_2]_{0.75}[Ac]_{0.25}$	$[C_2mim][NTf_2]_{0.25}[Ac]_{0.75}$
293.15	38.600	103.633	29.169	98.011	60.936	127.927
298.15	32.023	79.097	24.537	75.559	48.950	95.812
303.15	26.897	61.728	20.878	59.471	39.967	73.507
308.15	22.855	49.137	17.963	47.661	33.102	57.596
313.15	19.645	39.812	15.603	38.804	27.767	45.972
318.15	17.053	32.787	13.662	32.066	23.561	37.323
323.15	14.918	27.354	12.071	26.848	20.202	30.750
328.15	13.158	23.117	10.731	22.732	17.480	25.681
333.15	11.687	19.744	9.605	19.452	15.261	21.697
338.15	10.447	17.024	8.647	16.807	13.425	18.527
343.15	9.394	14.811	7.827	14.648	11.859	15.976

Table S10| Calculated viscosity deviations, $\Delta\eta$ (mPa s), of the ionic liquid mixtures at 293.15 K.

T (K)	$[C_2mim][NTf_2]_{0.5}[SCN]_{0.5}$	$[C_2mim][NTf_2]_{0.5}[Lac]_{0.5}$	$[C_2mim][NTf_2]_{0.5}[N(CN)_2]_{0.5}$	$[C_2mim][NTf_2]_{0.5}[Ac]_{0.5}$	$[C_2mim][NTf_2]_{0.75}[Ac]_{0.25}$	$[C_2mim][NTf_2]_{0.25}[Ac]_{0.75}$
293.15	0.1571	-0.1493	0.0965	0.1995	0.0841	0.1059
298.15	0.1499	-0.1226	0.0926	0.1946	0.0861	0.1065
303.15	0.1449	-0.0987	0.0915	0.1910	0.0900	0.1065
308.15	0.1378	-0.0810	0.0882	0.1841	0.0891	0.1039
313.15	0.1315	-0.0667	0.0846	0.1765	0.0872	0.1007
318.15	0.1262	-0.0544	0.0809	0.1692	0.0849	0.0971
323.15	0.1203	-0.0452	0.0779	0.1620	0.0822	0.0931
328.15	0.1147	-0.0375	0.0740	0.1541	0.0785	0.0890
333.15	0.1097	-0.0317	0.0712	0.1468	0.0756	0.0845
338.15	0.1028	-0.0299	0.0658	0.1374	0.0688	0.0787
343.15	0.0982	-0.0268	0.0627	0.1306	0.0625	0.0742

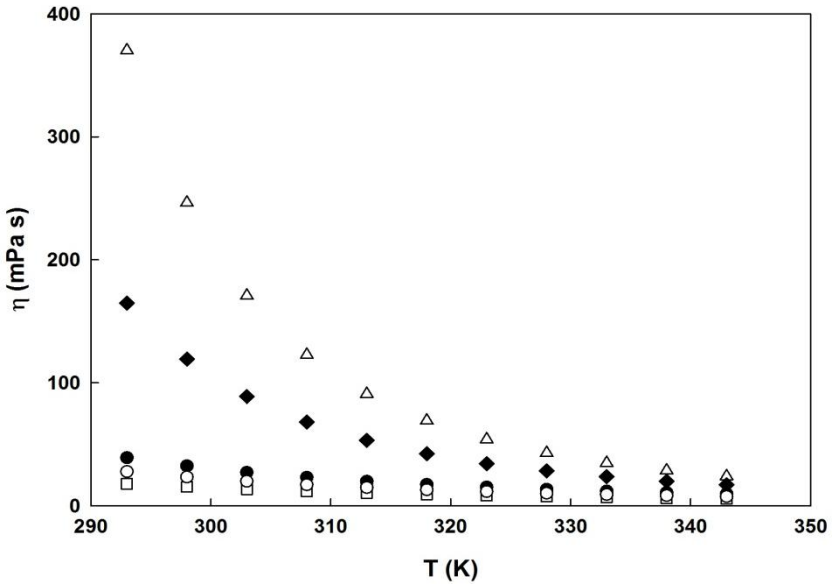

Figure S4| Experimental viscosities of the pure ionic liquids: $[C_2mim][NTf_2]$(●), $[C_2mim][Ac]$ (♦), $[C_2mim][N(CN)_2]$ (□), $[C_2mim][Lac]$ (Δ), $[C_2mim][SCN]$ (○).

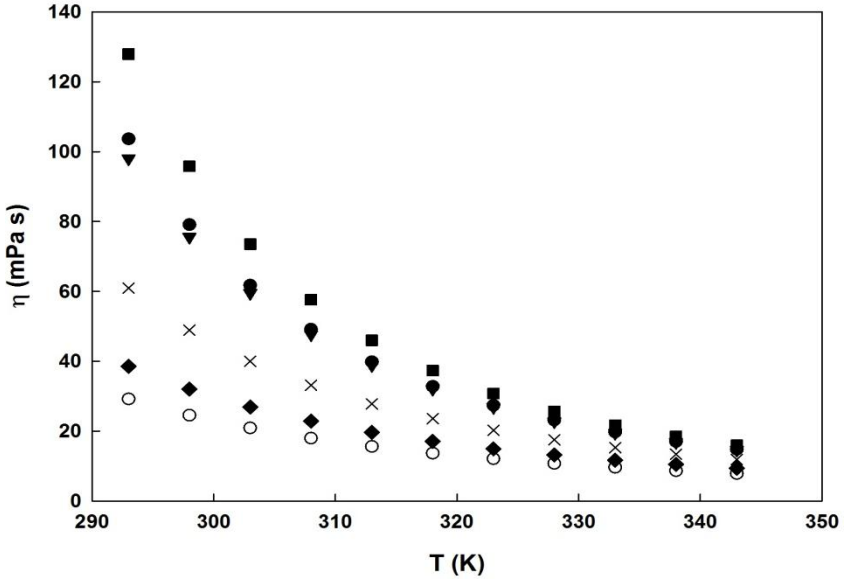

Figure S5| Experimental viscosities of the ionic liquid mixtures: $[C_2mim][NTf_2]_{0.5}[Lac]_{0.5}$ (●), $[C_2mim][NTf_2]_{0.5}[Ac]_{0.5}$ (▼), $[C_2mim][NTf_2]_{0.75}[Ac]_{0.25}$ (x), $[C_2mim][NTf_2]_{0.25}[Ac]_{0.75}$ (■), $[C_2mim][NTf_2]_{0.5}[N(CN)_2]_{0.5}$ (○), $[C_2mim][NTf_2]_{0.5}[SCN]_{0.5}$ (♦).

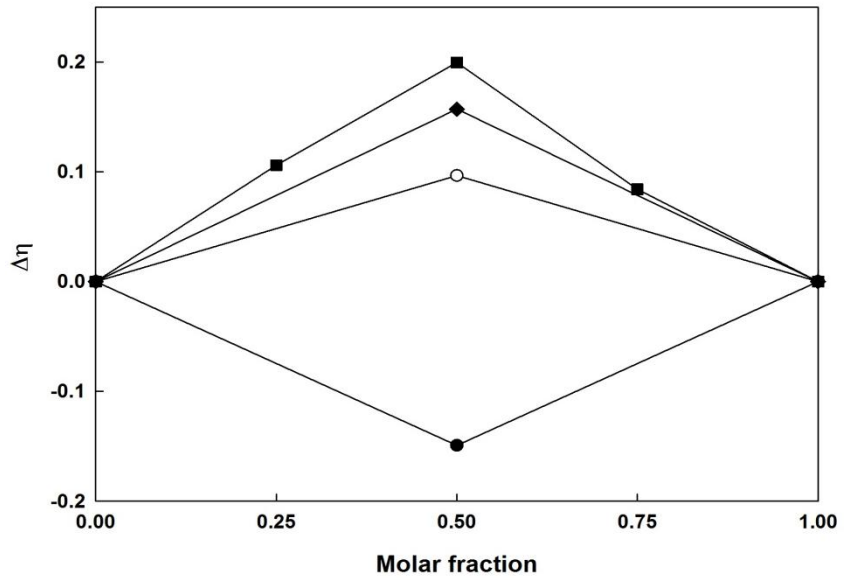

Figure S6| Viscosity deviations of the ionic liquid mixtures at 293.15 K: $[C_2mim][NTf_2][Lac]$ (●), $[C_2mim][NTf_2][Ac]$ (■), $[C_2mim][NTf_2][N(CN)_2]$ (○), $[C_2mim][NTf_2][SCN]$ (♦).

Table S11| Fitted parameters of the linear expression given by Equation (S4).

Ionic liquid sample	ln(a)	$-E_a/R$	$-E_a$ (kJ mol^{-1})	r^2
$[C_2mim][NTf_2]$	-5.93 ± 0.15	2801 ± 47	23.3	0.9975 ± 0.0245
$[C_2mim][Ac]$	-10.42 ± 0.33	4525 ± 104	37.6	0.9952 ± 0.0546
$[C_2mim][Lac]$	-12.84 ± 0.48	5459 ± 153	45.4	0.9930 ± 0.0797
$[C_2mim][SCN]$	-5.67 ± 0.12	2627 ± 38	21.8	0.9981 ± 0.0201
$[C_2mim][N(CN)_2]$	-5.11 ± 0.10	2337 ± 32	19.4	0.9983 ± 0.0167
$[C_2mim][NTf_2]_{0.5}[SCN]_{0.5}$	-6.04 ± 0.13	2832 ± 42	23.6	0.9980 ± 0.0219
$[C_2mim][NTf_2]_{0.5}[Lac]_{0.5}$	-8.70 ± 0.25	3889 ± 77	32.3	0.9964 ± 0.0405
$[C_2mim][NTf_2]_{0.5}[N(CN)_2]_{0.5}$	-5.66 ± 0.12	2637 ± 37	21.9	0.9982 ± 0.0193
$[C_2mim][NTf_2]_{0.5}[Ac]_{0.5}$	-8.46 ± 0.22	3805 ± 70	31.6	0.9970 ± 0.0365
$[C_2mim][NTf_2]_{0.75}[Ac]_{0.25}$	-7.11 ± 0.16	3275 ± 51	27.2	0.9978 ± 0.0269
$[C_2mim][NTf_2]_{0.25}[Ac]_{0.75}$	-9.41 ± 0.26	4161 ± 83	34.6	0.9964 ± 0.0436

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Chapter 3

Part II: Mixing sulfate and cyano-functionalized anions

Adapted from: **L.C. Tomé,** C. Florindo, C.S.R. Freire, L.P.N. Rebelo, I.M. Marrucho, Palying with ionic liquid mixtures to design engineered CO_2 separation membranes, *Phys. Chem. Chem. Phys.*, 2014, **3**, 17172 – 17182.

The author contributed to the planning and execution of all the experiments presented, as well as on the discussion and preparation of the manuscript. The density and viscosity measurements were performed in collaboration with C. Florindo.

1. Abstract

Ionic liquids (ILs) have been explored as attractive alternative media for CO_2 separation not only due to their low volatility but also to their highly tunable nature. Aiming at designing highly efficient liquid phases for flue gas separation and natural gas purification, this work focuses on the use of binary IL mixtures containing sulfate and/or cyano-functionalized anions. Several mixtures were prepared and their gas transport properties through supported ionic liquid membranes (SILMs) were investigated. The thermophysical properties of those mixtures, namely viscosity and density, were also measured. The results indicate that depending on the anions mixed, membranes with fine-tuned gas permeabilities, diffusivities and solubilities can be obtained. Additionally, SILMs prepared with these IL mixtures are on the upper bound of the CO_2/N_2 separation, or even may surpass it, indicating their potential for separating CO_2 in low-pressure post-combustion processes. Overall, the use of IL mixtures combining the most selective anions with the least viscous anions is a highly promising strategy to design advanced engineered liquid phases for CO_2 separation membranes.

2. Introduction

In the last decade, ILs have finding their unquestionable place in modern chemistry as new functional materials. They have been advantageously used to promote more efficient processes or deliver better products in a plethora of different applications such as solvents for biological molecules[1-3] and plant macromolecular components like cellulose,[4] lignin,[5] and cork,[6] in batteries and fuel cells,[7] or carbon capture processes.[8] Most of these applications are related to the implementation of newly proposed green chemistry regulations, which have offered the opportunity to re-thinking chemical processes and products in terms

of efficiency. Ionic liquids are low-melting-point salts with an exceptional combination of properties such as negligible vapor pressure,[9] high thermal stability,[10] and low flammability.[11] However, their most important feature is the capability to tailor many of their physical and chemical properties by combining different cations and anions or by adding functional groups. This fact makes them absolutely unique and incomparable to other solvents, and most of their success, stems from this property.

One of the most active areas of research regarding ILs is their use in the development of efficient and economic separation processes. Due to the good levels of solubility and selectivity of CO_2 in these fluids over other light gases, as well as their low volatility and highly tunable nature, there has been a growing interest in the exploitation of ILs as alternative media for CO_2 capture and separation processes applying different approaches, namely as liquid absorbers and supported liquid membranes.[12-20]

Brennecke and co-authors thoroughly studied the CO_2 solubility in several commonly used ILs and concluded that the anion has a dominant role on CO_2 solubility.[21-24] The influence of different functional groups, such as alkyl, ether, hydroxyl, amine, ethylene glycol, nitrile and fluorinated, on the gas solubility properties of ILs has also been intensively investigated by different authors.[25-31] In fact, a quick search in the literature on the subject of CO_2 solubility in ILs clearly shows the chemical diversity of the ILs studied up to now. From amine inspired reactive ILs to aprotic heterocyclic anion ILs,[32] the most recent studies focus on task-specific ILs by using basic anions, such as acetate,[33, 34] amino acids,[35, 36] imidazolide or pyrrolide.[37]

Supported ionic liquid membranes, where the desired IL is immobilized into the pores of a solid membrane by capillary forces,[13] are a very attractive strategy compared to bulk-fluid ILs not only due to the smaller amounts of IL needed but also because membrane technology offers significant low energy consumption

and operating costs.[38] Consequently, a broad diversity of ILs has also been used to develop SILMs for CO_2 separation. Several studies on gas permeation properties through SILMs have investigated the effect of the IL chemical structure, covering diverse cations, such as imidazolium,[39-56] pyrrolidinium,[56-59] piperidinium and morpholinium,[58] pyridinium,[59-61] ammonium,[61, 62] phosphonium,[63-67] thiazolium,[68, 69] or cholinium,[70] combined with halogens, fluorinated anions, sulfonates, carboxylates, amino acids, tosylate and cyano-containing anions. Different structural variations of the imidazolium cation have also been explored in order to tune the CO_2 selectivity of SILMs. For instance, Bara *et al.* synthesized ILs containing fluoroalkyl imidazolium-based cations and observed that the CO_2/CH_4 ideal selectivities of these ILs are higher than those of their alkyl analogues.[71] Hanioka *et al*. showed that SILMs of amine-functionalized imidazolium ILs are highly selective in CO_2/CH_4 separation due to facilitated CO_2 transport.[72] Myers *et al.* also reported high CO_2/H_2 separation performances at high temperatures of a supported amine-functionalized IL membrane.[73]

Ionic liquid mixtures offer a mean to further increase flexibility and fine-tune capacity of the physical and chemical properties of ILs, providing an extra degree of freedom for designing new solvents.[74-76] We have recently proposed the use of IL mixtures to prepare SILMs for CO_2 separation, fixing the 1-ethyl-3-methylimidazolium cation ($[C_2mim]^+$) and researching only on the anion chemical structure.[77] Although higher CO_2 solubility selectivity improvements were obtained by mixing acetate or lactate with the bis(trifluoromethylsulfonyl)imide anion, the presence of the former anions decreased the gas permeability through the prepared SILMs, essentially due to the high viscosities of the ILs containing the carboxylated anions. However, high CO_2 separation performances were found for IL mixtures containing anions with cyano groups, namely dicyanamide and thiocyanate, which were the less viscous ILs used. In sum, the results obtained showed that a proper balance combining both the most CO_2 selective and the less

viscous anions is crucial to achieve improved CO_2 separation performances.[77] All the above mentioned aspects motivated us to further investigate the tailoring power of binary IL mixtures and its effect on the CO_2 separation performance of SILMs. Taking into account that the anions of ILs have a stronger influence on CO_2 solubility than the cations [24] and that the CO_2 molecules have a larger affinity for anion *versus* cation associations,[19] IL mixture systems with a common cation and different anions were here explored. Six ILs having $[C_2mim]^+$ combined with different sulfate- and cyano-functionalized anions, namely methylsulfate ($[C_1SO_4]$), ethylsulfate ($[C_2SO_4]^-$), thiocyanate ($[SCN]^-$), dicyanamide ($[N(CN)_2]^-$), tricyanomethane ($[C(CN)_3]^-$) and tetracyanoborate ($[B(CN)_4]^-$), were mixed and their CO_2, CH_4, and N_2 permeation properties through SILMs determined. The chemical structures of the ILs used are presented in Figure 1. Although Finotello *et al*. have previously showed that an imidazolium-based IL with the methylsulfate anion present high CO_2/N_2 and CO_2/CH_4 solubility selectivities compared to those of ILs with fluorinated anions,[78] SILMs based on ionic liquids with sulfate anions are reported herein for the first time. Regarding the ILs with the cyano-functionalized anions, they were chosen not only due to their high CO_2 permeabilities and selectivities,[49, 56, 77] but also because of their remarkable low viscosities.[79] Since both the IL viscosity and molar volume are important parameters that impact the gas permeation properties of SILMs, the thermophysical properties, namely density and viscosity, of the pure ILs and the prepared binary IL mixtures were also measured.

3. Experimental Section

3.1. Materials

IoLiTec GmbH provided the 1-ethyl-3-methylimidazolium methylsulfate ($[C_2mim][C_1SO_4]$) (99 wt% pure), 1-ethyl-3-methylimidazolium dicyanamide

([C_2mim][$N(CN)_2$]) (> 98 wt% pure), and 1-ethyl-3-methylimidazolium tricyanomethane ([C_2mim][$C(CN)_3$]) (> 98 wt% pure). Fluka supplied the 1-ethyl-3-methylimidazolium thiocyanate ([C_2mim][SCN]) (≥ 95 wt% pure). The 1-ethyl-3-methylimidazolium ethylsulfate ([C_2mim][C_2SO_4]) (≥ 99 wt% pure), and the 1-ethyl-3-methylimidazolium tetracyanoborate ([C_2mim][$B(CN)_4$]) (> 98 wt% pure), were purchased from Merck KGaA Germany. To reduce the water and other volatile substances content, all the pure IL samples were dried under vacuum (10^{-3} kPa) and subject to vigorous stirring at a moderated temperature (≈ 318 K) for at least 4 days immediately prior to use. The water contents of the pure ILs, determined by Karl Fischer titration (831 KF Coulometer, Metrohm), are presented in Table 1. No further purification of the ILs was carried out, but their purities were further evaluated by ^{1}H and ^{13}C RMN analysis and were found to be in accordance with the levels given by the suppliers.

The IL + IL mixtures were prepared using an analytical high-precision balance with an uncertainty of ± 10^{-5} g by syringing known masses of the IL components into glass vials. Good mixing was assured by magnetic stirring for at least 30 minutes. Then, the prepared IL mixtures were dried under vacuum (10^{-3} kPa) at a moderate temperature (≈ 318 K) for another 4 days. The samples were prepared immediately prior to the measurements to avoid variations in composition. The composition descriptions of the prepared IL + IL mixtures, as well as their water contents are also presented in Table 1.

3.2. Viscosity and density determination

Measurements of viscosity and density of the pure ILs and their mixtures were performed in the temperature range between 293.15 and 353.15 K at atmospheric pressure using an SVM 3000 Anton Paar rotational Stabinger viscometer-densimeter. The SVM 3000 uses Peltier elements for fast and efficient thermostability and the temperature uncertainty is ± 0.02 K. The precision of the

dynamic viscosity measurements is ± 0.5% and the absolute uncertainty of the density is ± 0.0005 g cm^{-3}. The overall uncertainty of the viscosity measurements (taking into account the purity and handling of the samples) was estimated to be 2%.[80] Triplicates of each sample were performed to ensure accuracy and the reported results are the average values.

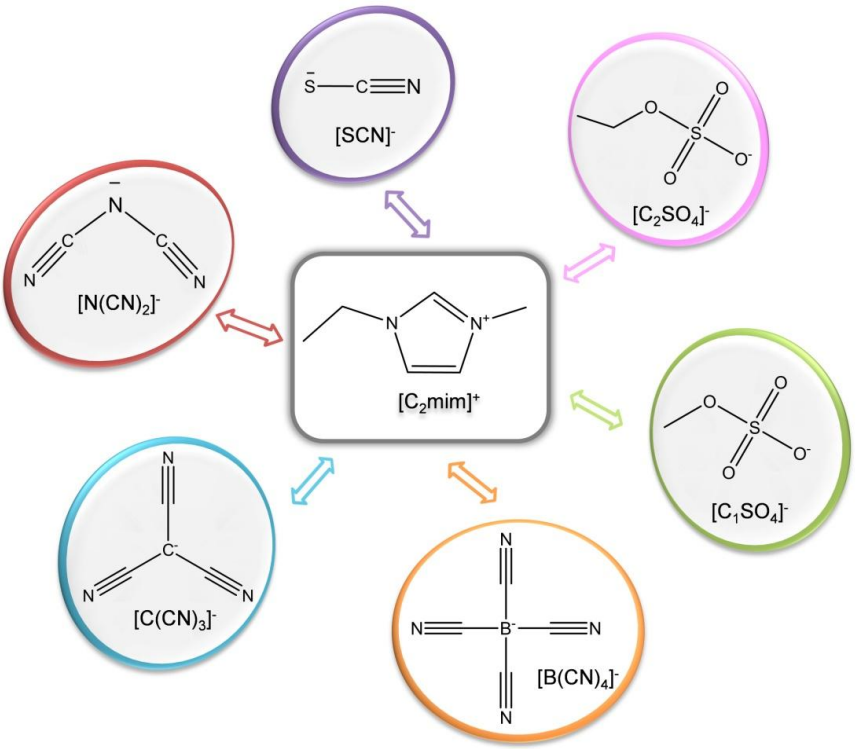

Figure 1| Chemical structures of the cation and anions used in this study.

3.3. Gas permeation measurements

Porous hydrophilic poly(tetrafluoroethylene) (PTFE) membranes provided by Merck Millipore, with a pore size of 0.2 µm and average thickness of 65 µm, were used to prepare all the SILM configurations according to our previously reported procedure.[77]

Gas permeabilities and diffusivities through the prepared SILMs were measured using a time-lag apparatus, construction and operation details on which are entirely described elsewhere.[57] In the present work, each prepared SILM was positioned on the top of a highly porous sintered disk for providing mechanical stability and installed into the flat-type permeation cell where it was degassed under vacuum during 12 hours before testing. The single gas permeation measurements using CO_2, CH_4, and N_2, were conducted at 293 K with an upstream pressure of 100 kPa against initial vacuum downstream (< 0.1 kPa). At least three separate experiments of each gas on a single SILM sample were performed. Between experiments, the permeation cell and lines were evacuated on both upstream and downstream sides until the pressure was below 0.1 kPa. No residual ionic liquid was found inside the permeation cell at the end of the experiments and, correspondingly, the membrane mass remained constant throughout the experiment. The thickness of the SILMs was assumed to be equivalent to the membrane filter thickness.

The gas transport through a liquid membrane occurs according a solution-diffusion mass transfer mechanism where the permeability (*P*) is related to solubility (*S*) and diffusivity (*D*) as follows:[81]

$$P = S \times D \tag{1}$$

Permeability (*P*) is defined as the steady-state gas flux (*J*) through a membrane under a transmembrane pressure drop (Δp) and normalized to the unit thickness of the membrane as follows:[82]

$$P = J \frac{\ell}{\Delta p} \tag{2}$$

The flux was determined experimentally using Equation 3, where V^p is the permeate volume, Δp_d is the variation of downstream pressure, *A* is the effective

membrane surface area, *t* is the experimental time, *R* is the Ideal Gas Law constant and *T* is the absolute temperature.

$$J = \frac{V^p \Delta p_d}{AtRT} \tag{3}$$

Diffusivity (*D*) was obtained according to Equation 4. The time-lag parameter (θ), which can be obtained before achieving steady-state flux, was deduced by extrapolating the slope of the linear portion of the p_d vs. *t* curve back to the time axis, where the intercept is equal to θ.[83]

$$D = \frac{\ell^2}{6\theta} \tag{4}$$

After knowing both *P* and *D*, it was also possible to calculate *S* using the relationship shown in Equation (1).

The ideal permeability selectivity (or permselectivity), $\alpha_{i/j}$, was obtained by dividing the permeability of the more permeable specie *i* to the permeability of the less permeable specie *j*. As shown in Equation (5), the permselectivity can also be expressed as the product of the diffusivity selectivity and the solubility selectivity.

$$\alpha_{i/j} = \frac{P_i}{P_j} = \left(\frac{D_i}{D_j}\right) \times \left(\frac{S_i}{S_j}\right) \tag{5}$$

Table 1| Composition descriptions and physical properties of the pure ionic liquids and their mixtures used to prepare the SILMs.

Ionic liquid sample	Composition (Mole fraction)	wt% of water	M (g mol^{-1})	η [a] (MPa s)	ρ [a] (g cm^{-3})	V_m [b] (cm^3 mol^{-1})
$[C_2mim][C_1SO_4]$	pure	0.01	222.07	127.523	1.294	171.62
$[C_2mim][C_2SO_4]$	pure	0.03	236.08	119.987	1.241	190.26
$[C_2mim][SCN]$[c]	pure	0.09	169.25	27.846	1.119	151.24
$[C_2mim][N(CN)_2]$[c]	pure	0.09	177.21	17.947	1.106	160.24
$[C_2mim][C(CN)_3]$	pure	0.01	201.23	16.624	1.085	185.54
$[C_2mim][B(CN)_4]$	pure	0.01	236.05	21.434	1.040	226.89
$[C_2mim][C_1SO_4]_{0.5}[SCN]_{0.5}$	$x[C_2mim][C_1SO_4]=0.5 + x[C_2mim][SCN]=0.5$	0.08	195.66	60.380	1.211	161.55
$[C_2mim][C_1SO_4]_{0.5}[N(CN)_2]_{0.5}$	$x[C_2mim][C_1SO_4]=0.5 + x[C_2mim][N(CN)_2]=0.5$	0.03	199.64	49.200	1.203	165.94
$[C_2mim][C_1SO_4]_{0.5}[C(CN)_3]_{0.5}$	$x[C_2mim][C_1SO_4]=0.5 + x[C_2mim][C(CN)_3]=0.5$	0.03	211.59	41.022	1.179	179.41
$[C_2mim][C_1SO_4]_{0.5}[B(CN)_4]_{0.5}$	$x[C_2mim][C_1SO_4]=0.5 + x[C_2mim][B(CN)_4]=0.5$	0.02	229.06	53.726	1.144	200.24
$[C_2mim][SCN]_{0.5}[N(CN)_2]_{0.5}$	$x[C_2mim][SCN]=0.5 + x[C_2mim][N(CN)_2]=0.5$	0.04	173.23	21.287	1.112	155.85
$[C_2mim][SCN]_{0.5}[C(CN)_3]_{0.5}$	$x[C_2mim][SCN]=0.5 + x[C_2mim][C(CN)_3]=0.5$	0.02	185.18	20.711	1.099	168.48
$[C_2mim][SCN]_{0.5}[B(CN)_4]_{0.5}$	$x[C_2mim][SCN]=0.5 + x[C_2mim][B(CN)_4]=0.5$	0.02	202.65	23.233	1.070	189.34

[a] Viscosity (η) and density (ρ) measured at 293.15 K.

[b] Molar volume (V_m) obtained for 293.15 K.

[c] Values taken from Tomé *et al*.[77]

4. Results and Discussion

The structures of the pure ILs used and the composition description of the prepared IL + IL mixtures are shown in Figure 1 and Table 1, respectively. The viscosity and density values reported in Table 1 were measured in this work and a detail description of these data, in a temperature range from 293.15 and 353.15 K, is presented and discussed in Supplementary Information.

4.1. Gas permeability

The gas permeabilities through the prepared SILMs, measured at 293 K with a transmembrane pressure differential of 100 kPa, are shown in Figure 2. To the best of our knowledge, the gas permeation properties of $[C_2mim][C_1SO_4]$, $[C_2mim][C_2SO_4]$ and $[C_2mim][C(CN)_3]$-based SILMs are here reported for the first time. Both the pure $[C_2mim][SCN]$ and $[C_2mim][N(CN)_2]$-based SILMs were previously determined by us using the same experimental conditions.[77] Concerning the pure $[C_2mim][B(CN)_4]$-based SILM, a comparison of CO_2 and N_2 permeabilities measured in this work with the values first reported by Mahurin *et al*.[49] is shown in Table 2. The large differences between CO_2 and N_2 permeabilities can be explained by the different measurement conditions as well as the different membrane supports used. The experimental methods used in the present work minimized the water content since all the IL samples were dried under vacuum for 4 days, the SILMs were prepared under dry conditions and vacuum was applied to the membranes inside the permeation cell for 12 hours, until a constant pressure was obtained, before starting the gas experiments. Since Mahurin *et al*.[49] did not report the water content and the purity of the $[C_2mim][B(CN)_4]$ used, an exact comparison of the results cannot be made. Still, it is worth noting that the pure $[C_2mim][C(CN)_3]$ and $[C_2mim][B(CN)_4]$-based SILMs measured in this work present higher CO_2 permeabilities (667 and 742 Barrer, respectively) compared to the

$[C_2mim][NTf_2]$ (589 Barrer),[77] which is known to has the highest permeability among pure SILMs.[13]

Table 2| Comparison of CO_2 and N_2 permeabilities measured in this work with values reported in literature.

$[C_2mim][B(CN)_4]$	This work	Mahurin *et al.*[49]
Membrane support	Hydrophilic PTFE	Anodic Alumina
Measurement conditions	293 K and 100 kPa	298 K and 35 kPa
CO_2 permeability (Barrer)	742	2040
N_2 permeability (Barrer)	15.1	38
Water content (wt%)	0.01	N/A
Purity (wt%)	98	N/A

Figure 2 shows that the same trend of gas permeability values was observed for all the SILMs tested: $P\ CO_2 >> P\ CH_4 > P\ N_2$. The CO_2 permeability values obtained vary from 742 to 111 Barrer, while for CH_4 and N_2 they range from 1.6 to 39 Barrer. In fact, the CO_2 permeability is always one or two orders of magnitude higher than that of CH_4 and N_2, indicating SILMs aptitude to separate these gases. Regarding the anion chemical nature of the ILs, it can be observed that the pure SILMs based on the sulfate anions present lower gas permeabilities than the pure SILMs containing cyano-functionalized anions (Figure 2). This behavior is probably due to the higher viscosities of ILs containing sulfate anions compared to those with cyano-functionalized anions, which have remarkable low viscosities (Table 1). Likewise, the gas permeabilities through the pure SILMs increase when methylsulfate is replaced by the less viscous ethylsulfate anion (Figure 2). This general trend scaling the gas permeability with IL viscosity has been recognized by different authors.[13, 49, 59, 66, 68, 84] However, analyzing the results obtained for the ILs containing –CN groups, the CO_2 permeabilities greatly increase (from 263 to 742 Barrer) with the increasing number of cyano groups $[SCN]^- < [N(CN)_2]^- < [C(CN)_3]^- <$

$[B(CN)_4]^-$ in the IL anion (Figure 2), contrasting with the IL viscosity trend $[SCN]^-$ > $[B(CN)_4]^-$ > $[N(CN)_2]^-$ > $[C(CN)_3]$ (Table 1). This is evidence that the description of gas permeability simply in terms of IL viscosity does not provide a full understanding of SILMs based on the cyano-functionalized anions.

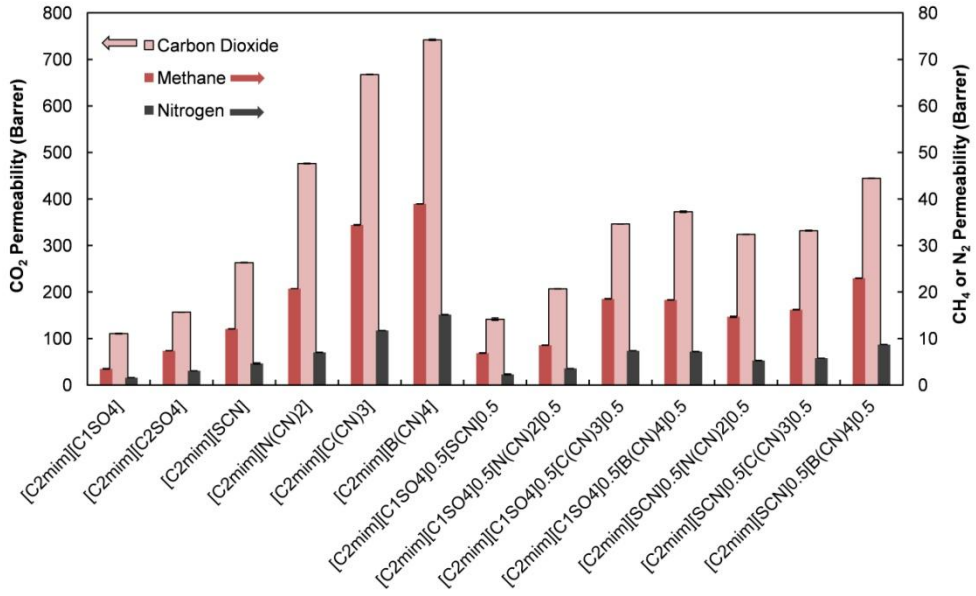

Figure 2| Gas permeabilities (1 Barrer = 10^{-10} cm^3(STP)cm cm^{-2} s^{-1} $cmHg^{-1}$) through the prepared SILMs. Error bars represent standard deviations based on three experimental replicas. The gas permeability values of $[C_2mim][SCN]$ and $[C_2mim][N(CN)_2]$-based SILMs were taken from Tomé *et al*.[77]

Regarding the IL mixtures, mixing different ILs having cyano-functionalized anions with the $[C_2mim][C_1SO_4]$ has significant influence on the gas permeability properties of the SILMs. For instance, the addition of 0.5 mole fraction of $[C_2mim][SCN]$ to $[C_2mim][C_1SO_4]$ increases CO_2, CH_4, and N_2 permeabilities by 28%, 97% and 44%, respectively, while, if 0.5 mole fraction of $[C_2mim][B(CN)_4]$ is added, permeability enhancements of roughly 236%, 423% and 350% occurred. Similarly, mixing 0.5 mole fraction of $[C_2mim][B(CN)_4]$ with $[C_2mim][SCN]$ increases 69%, 90% and 89% the CO_2, CH_4, and N_2 permeabilities compared to those of the pure $[C_2mim][SCN]$-based SILM. However, mixing 0.5 mole fraction $[C_2mim][N(CN)_2]$ or

$[C_2mim][C(CN)_3]$ with $[C_2mim][SCN]$ promotes similar increments of CO_2, CH_4, and N_2 permeabilities through the corresponding SILMs (Figure 2). In summary, mixing cyano-functionalized ILs has a great impact on the gas permeability properties of ensuing SILMs.

4.2. Gas diffusivity

The experimental gas diffusivities obtained in this work are plotted in Figure 3. It can be observed that the SILMs with the lowest gas diffusivities are $[C_2mim][C_1SO_4]$ and $[C_2mim][C_2SO_4]$, which have the lowest gas permeabilities (Figure 2) and also the highest viscosities (Table 1). Conversely, $[C_2mim][C(CN)_3]$, the less viscous IL (16.624 mPa s), presents the highest gas diffusivities but the highest gas permeabilities belong to the pure $[C_2mim][B(CN)_4]$-based SILM. A similar unexpected behavior can also be observed for SILMs made of IL mixtures. While the $[C_2mim][SCN]_{0.5}[B(CN)_4]_{0.5}$ mixture has the highest gas permeabilities amongst the mixtures of $[SCN]^-$ with the other cyano-functionalized anions (Figure 2), it also presents lower gas diffusivities (Figure 3) and higher viscosities (Table 1) compared to both $[C_2mim][SCN]_{0.5}[N(CN)_2]_{0.5}$ and $[C_2mim][SCN]_{0.5}[C(CN)_3]_{0.5}$-based SILMs. Thus, the gas permeabilities through the prepared SILMs are not entirely controlled by their gas diffusivities and the respective IL viscosities, meaning that gas solubilities should also be considered.

Several correlations for gas diffusivities in ILs have been developed considering different parameters, namely the effect of temperature, gas molar volume, IL viscosity, IL density and IL molecular weight.[40, 60, 62, 63]

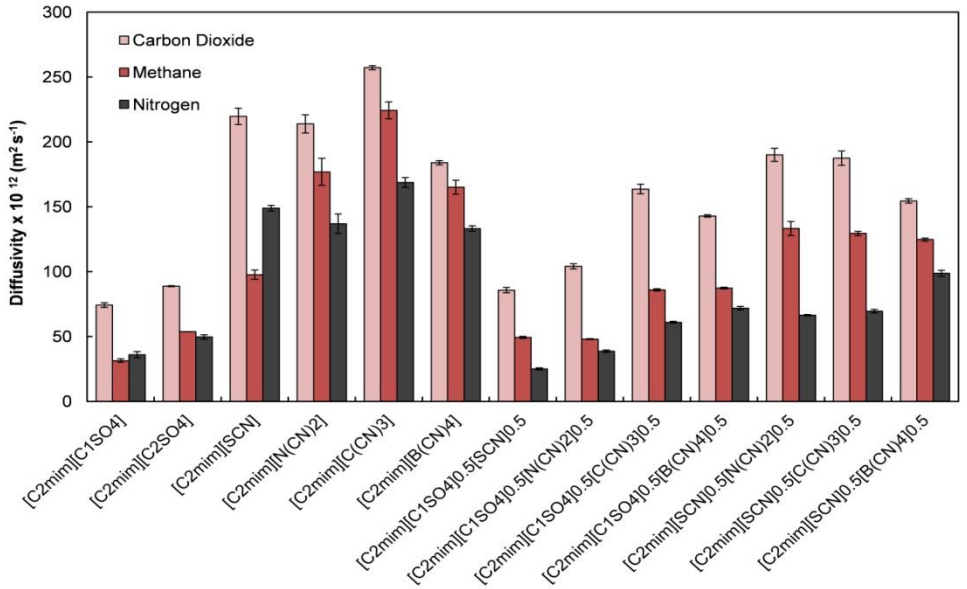

Figure 3| Gas diffusivities through the prepared SILMs. Error bars represent standard deviations based on three experimental replicas. The gas diffusivity values of $[C_2mim][SCN]$ and $[C_2mim][N(CN)_2]$-based SILMs were taken from Tomé *et al*.[77]

A general correlation, proposed by Scovazzo and co-authors, has been used in the following form:[13]

$$D = A\frac{V_{IL}^{a}}{\eta_{IL}^{b}V_{gas}^{c}} \tag{6}$$

where *A*, *a*, *b* and *c* are IL-class specific parameters, η_{IL} is the viscosity of the IL, V_{IL} is the IL molar volume and V_{gas} is the solute gas molar volume. For ILs with 1-alkyl-3-methylimidazolium cations having an alkyl chain length smaller than four carbon atoms, *a* is equal to zero,[13] and consequently the gas diffusivity is inversely proportional to the IL viscosity. In this context, the relationship between CO_2, CH_4, and N_2 diffusivity and the IL viscosity for the studied pure ILs and their binary mixtures are depicted in Figures 4(a), (b) and (c), respectively. For the three studied gases, a decrease in the mixture viscosity, due to the presence of 0.5 mole fraction of a less viscous ILs containing cyano-functionalized anion, corresponds to an increase in gas diffusivities. Thus, the lower the solvent viscosity, the faster the

gas passes through the SILM. This behavior, also observed for the pure SILMs measured in this work, is similar to the previously proposed trends observed for other SILMs.[13, 40, 62, 63]

The insets in Figure 4 allow a more quantitative evaluation of the gas diffusivity dependence on the IL viscosity, using a log–log plot. For imidazolium-based ILs, Morgan *et al*. [40] showed that gas diffusivity is inversely proportional to IL viscosity with an average power of 0.6. The fits depicted on the log–log plots of Figures 4 (a), (b) and (c), show that experimental CO_2, CH_4 and N_2 diffusivities of the pure ILs and their mixtures tested in this work vary inversely with IL viscosity to the powers of 0.529, 0.785 and 0.652, respectively. These power values are in reasonable agreement with literature values, given that the reported 0.6 power law is not a theoretical value but an empirical observation based on data for a series of pure imidazolium-ILs, which did not include sulfate or cyano anions.

4.3. Gas solubility

The CO_2, CH_4, and N_2 solubilities determined in this work using Equation (1) are shown in Figure 5. For all the prepared SILMs, CO_2 solubility is always greater than that of CH_4 and N_2. Actually, the same trend obtained for gas permeability (Figure 2, $P\ CO_2 >> P\ CH_4 > P\ N_2$) was also observed for gas solubility (Figure 5, $S\ CO_2 >> S\ CH_4 > S\ N_2$). Although the permeation of the gas molecules can be considered as a two step process, dissolution into the liquid phase and diffusion through it, the differences between the gas permeabilities mainly arise from the gas solubility differences. Consequently, the high CO_2 permeability compared to that of CH_4 and N_2 (Figure 2) can be essentially attributed to the high levels of CO_2 solubility, relate to CH_4 and N_2 (Figure 5).

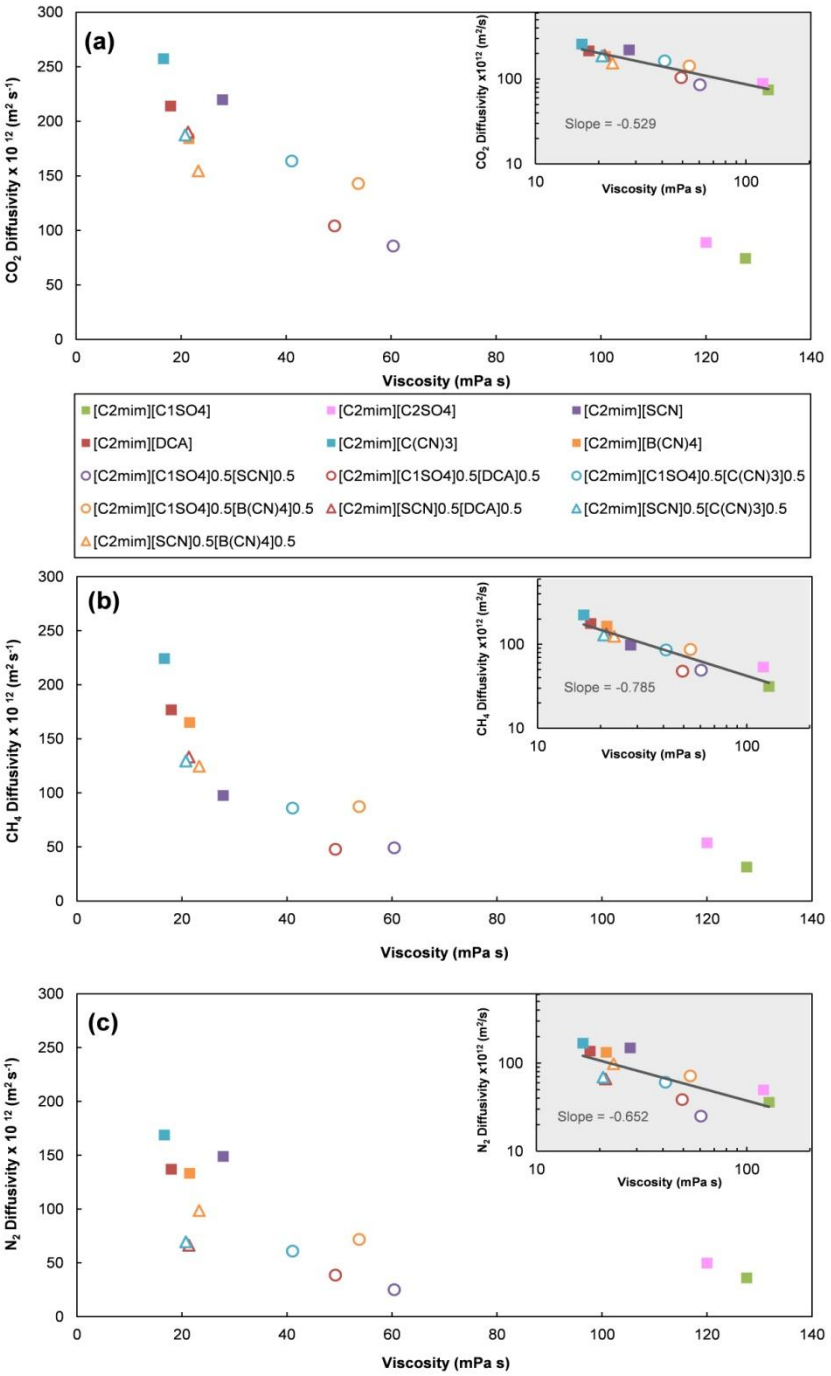

Figure 4| Experimental carbon dioxide (a), methane (b), and nitrogen (c) diffusivities in the SILMs as function of IL viscosity measured at 293 K. Note that the insects show the same data on log-log plots.

From Figure 5, it can be seen that $[C_2mim][B(CN)_4]$ exhibits the highest gas solubilities, while the lowest gas solubilities were obtained in the pure $[C_2mim][SCN]$ SILM. The gas solubilities in the studied cyano-functionalized ILs significantly increase in the order $[C_2mim][SCN] < [C_2mim][N(CN)_2] < [C_2mim][C(CN)_3] < [C_2mim][B(CN)_4]$, while the gas solubilities of pure sulfate-based ILs increase when the $[C_1SO_4]^-$ is replace by the $[C_2SO_4]^-$ anion. Concerning the IL mixtures, Figure 5 shows that the addition of 0.5 mole fraction of $[C_2mim][SCN]$ to $[C_2mim][C_1SO_4]$ has little effect in the gas solubilities, whereas the presence of 0.5 mole fraction of $[C_2mim][N(CN)_2]$, $[C_2mim][C(CN)_3]$ or $[C_2mim][B(CN)_4]$ increases 36%, 45%, and 82% the CO_2 solubility, respectively. In the same way, mixing 0.5 mole fraction of $[C_2mim][B(CN)_4]$ with $[C_2mim][SCN]$ promotes CO_2, CH_4 and N_2 solubilities increments of 100%, 66% and 100%, respectively, compared to those of pure $[C_2mim][SCN]$. Overall, the CO_2 permeabilities (Figure 2), not only in the pure ILs containing cyano anions but also in their mixtures, are related to their respective CO_2 solubilities (Figure 5), both following the order of the anions: $[SCN]^- < [N(CN)_2]^- < [C(CN)_3]^- < [B(CN)_4]^-$.

It has been recognized that gas solubility in SILMs is related to IL molar volume.[13] Different correlations for the gas solubility based on the regular solution theory, with direct application to SILMs, have been proposed. Camper *et al.*[85] developed a model for imidazolium-based ILs that uses only the IL molar volume to predict gas solubility and solubility selectivity. Kilaru *et al*. proposed two-parameters models, similar to that of Camper, where viscosity[86] and surface tension[87] are also considered in addition to IL molar volume. Afterward, Scovazzo[13] derived a correlation (the so-called Universal Model) from an extend set of experimental data covering different IL families like imidazolium, ammonium and phosphonium. The Universal Model proposed a minimal influence of IL viscosity on the gas solubility but a significant dependence on the IL molar volume, in consistency with the Camper Model. Accordingly, both models predict

an exponential increase in the solubility selectivity as the IL molar volume decreases.[13, 85]

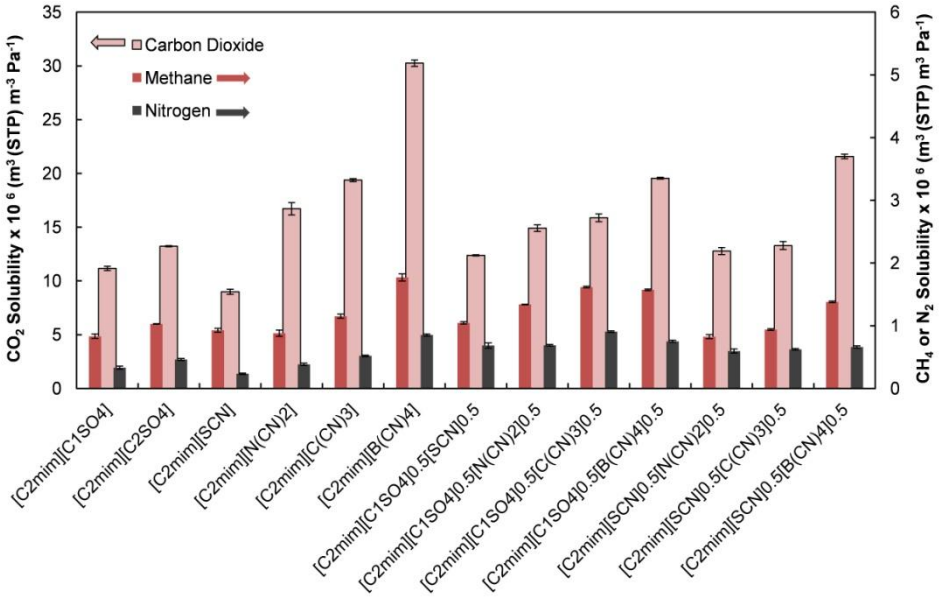

Figure 5| Gas solubilities in the SILMs studied, calculated using Equation (1). The gas solubility values of $[C_2mim][SCN]$ and $[C_2mim][N(CN)_2]$-based SILMs were taken from Tomé *et al*.[77]

Figure 6 displays the solubility selectivity values of the studied SILMs *versus* IL molar volume, as well as the fits of the Camper Model[83] and the Universal Model.[13] Looking at the pure SILMs with sulfate anions, it can be seen that the $[C_2mim][C_1SO_4]$, with lower molar volume, exhibits higher CO_2/N_2 and CO_2/CH_4 solubility selectivities compared to those of $[C_2mim][C_2SO_4]$. Also, the binary IL mixtures, containing the $[B(CN)_4]^-$ mixed with $[C_1SO_4]^-$ or $[SCN]^-$ anions are well described by both models (Figure 6). Nevertheless, deviations to both models are observed for SILMs based on IL mixtures containing the $[N(CN)_2]^-$ or the $[C(CN)_3]^-$ mixed with the $[C_1SO_4]^-$ or $[SCN]^-$ anions. Despite their lower molar volumes (Table 1), they have lowest CO_2/CH_4 and CO_2/N_2 solubility selectivities compared to those of the binary IL mixtures containing the $[B(CN)_4]^-$ anion (Figure 6). This outlier

behavior was also observed for the pure SILMs with the cyano-functionalized anions. Although their CO_2 solubilities (Figure 5) and molar volumes (Table 1) follow the order $[SCN]^-$ < $[N(CN)_2]^-$ < $[C(CN)_3]^-$ < $[B(CN)_4]$, the $[C_2mim][N(CN)_2]$-based SILM exhibited the highest CO_2/N_2 and CO_2/CH_4 solubility selectivities. This means that both models (Camper and Universal) are not entirely suitable to predict the solubility selectivities of all the SILMs, as claimed by Scovazzo.[13] In other words, the IL molar volume as a single parameter does not fully describe the solubility selectivity in SILMs, which is clearly in agreement to what was previously demonstrated for bulk-fluid ionic liquids by Shannon *et al*.[88]

In the same review,[13] Scovazzo affirmed that usually the permselectivity in SILMs is essentially dominated by solubility selectivity. Actually, the solubility selectivities in a SILM are accurate estimates of permselectivity, if its diffusivity selectivity is equal to the ratio of gas molar volumes, which is usually approximately one. This trend is well fitted to the experimental data used by Scovazzo's, who focused essentially on ILs based on fluorinated anions, namely $[NTf_2]^-$, $[PF_6]^-$, $[BF_4]^-$ and $[OTf]^-$.[13] The SILMs prepared in this work do not follow this trend. As it can be clearly seen, the permselectivities values (Figure 7(a)) are different from those of solubility selectivity (Figure 7(c)), due to the fact that the diffusivity selectivities are particularly higher than one (Figure 7(b)). These results, obtained for SILMs combining sulfate and/or cyano-based anions, show that permselectivities of SILMs cannot be universally estimated from their solubility selectivities. Deviations to this tendency were also observed for SILMs based on acetate and lactate anions.[77] All the mentioned evidences not only point out that the nature of the anions can highly influence the trends generally observed for SILMs, but also reaffirm that to better understand the mechanisms governing the gas permeation properties of SILMs is necessary to take into account the high diversity inherent to ILs.

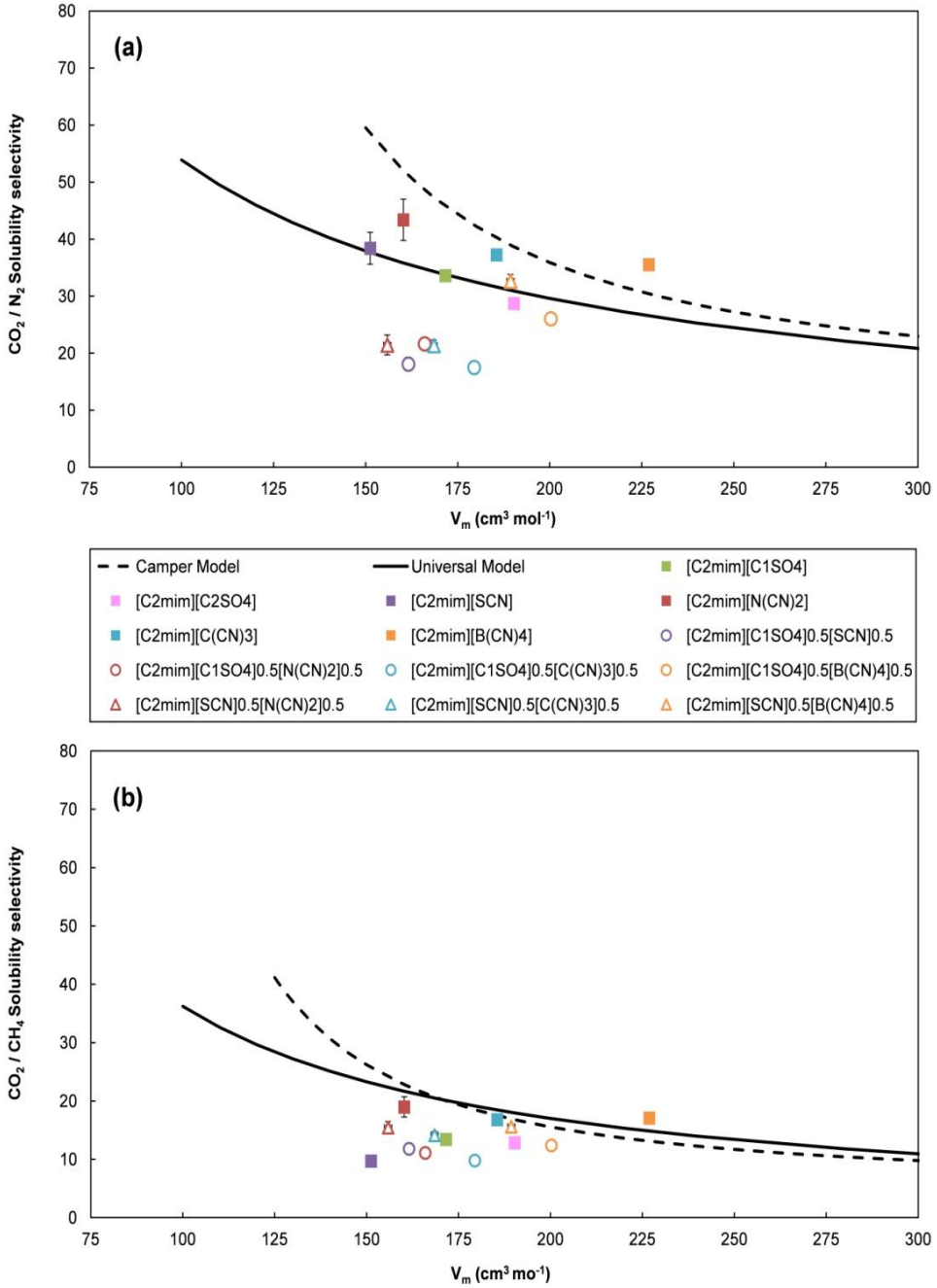

Figure 6| (a) CO_2/N_2 and (b) CO_2/CH_4 solubility selectivities of the prepared SILMs plotted *versus* IL molar volume. The error is either within the size of the markers or shown by error bars. The lines represent the solubility selectivity predicted by the Camper Model[85] and the Universal Model[13] for each gas pair.

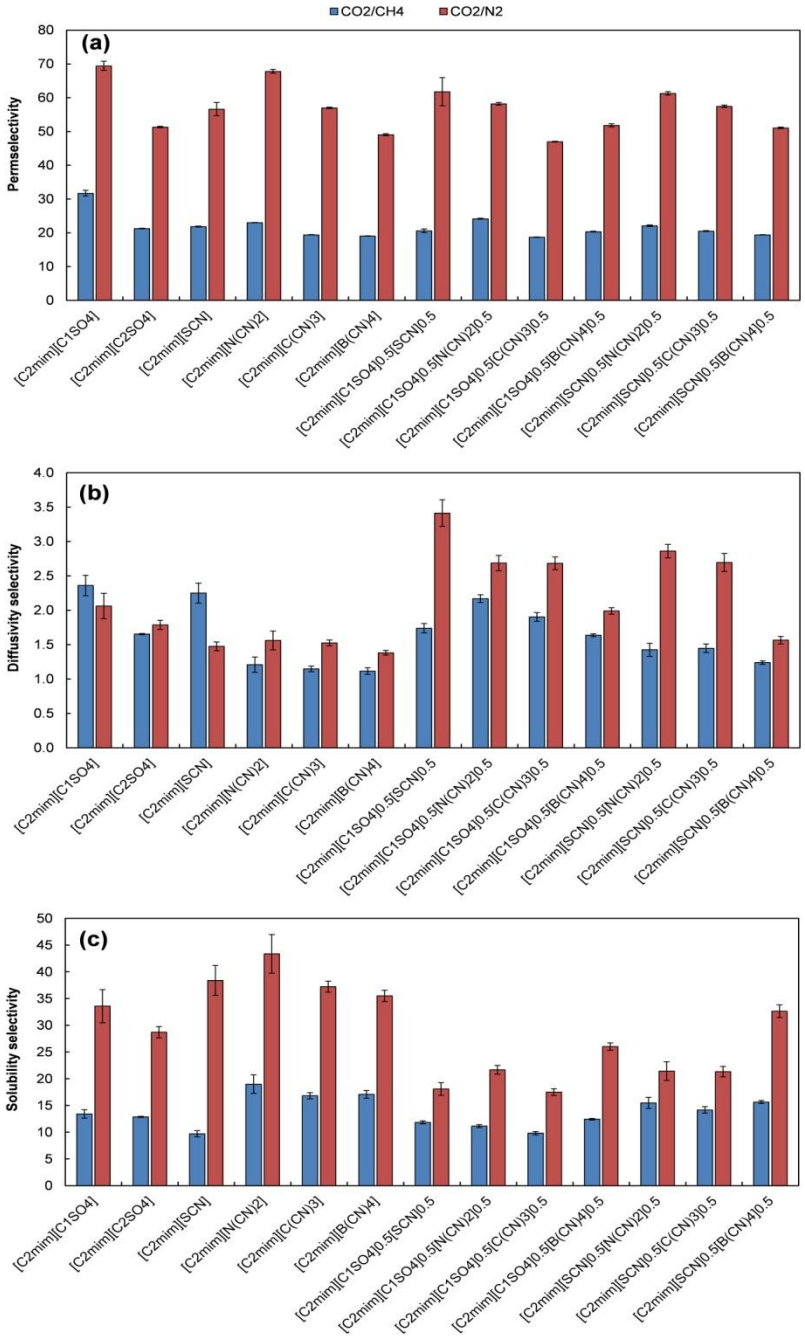

Figure 7| Permselectivity (a), diffusivity selectivity (b) and solubility selectivity (c) of the CO_2/CH_4 (blue bars) and CO_2/N_2 (red bars) in the prepared SILMs. The values of $[C_2mim][SCN]$ and $[C_2mim][N(CN)_2]$-based SILMs were taken from Tomé *et al*.[77]

4.4. CO_2 separation performance

The gas permeabilities and both the CO_2/CH_4 and CO_2/N_2 permselectivities values of the prepared SILMs are summarized in Table 3. The CO_2/CH_4 is always smaller than the CO_2/N_2 permselectivity since the CH_4 permeability is greater than that of N_2 in all the SILMs studied, including those made of IL + IL mixtures. This fact is in line with previous results reported for other pure SILMs.[13] As it can be seen in Table 3, among all the SILMs, the largest CO_2/CH_4 and CO_2/N_2 permselectivities, 31.7 and 69.4, respectively, were achieved for the pure $[C_2mim][C_1SO_4]$ SILM. Remarkably, these permselectivity values represent the highest values published so far for SILMs. The gas permeabilities through the membrane increased when the methylsulfate was replaced by ethylsulfate anion, whereas the pure $[C_2mim][C_2SO_4]$ SILM has significant lower permselectivities (CO_2/CH_4 = 21.2, CO_2/N_2 = 51.3,). For that reason, the $[C_2mim][C_1SO_4]$ was chosen to conduct the present study and mixed with the low viscous cyano-functionalized ILs.

In Figure 8, both the CO_2/CH_4 and CO_2/N_2 permselectivity values are plotted against CO_2 permeabilities on the so-called Robeson plots.[89] These plots, which are commonly used to evaluate the performance of membrane materials given a particular gas separation, illustrating the progress in membrane science, display the tradeoff line between permeability and selectivity for gas separation using polymeric membranes.[89] Since the performance of the vast majority of membranes falls below the upper bound, which is based on large amounts of experimental data for each separation, data points above this line can be considered as an improvement over the current membrane state of the art. Therefore, the comparison of CO_2/CH_4 and CO_2/N_2 separation performances between the results obtained in this work and the previously published data for SILMs can be evaluated, respectively, in Figure 8(a) and Figure 8(b).

Table 3| Single gas permeabilities (*P*, Barrer)[a] and ideal permselectivities (α) obtained for all the prepared SILMs.[b]

SILM sample	*P* CO_2	*P* CH_4	*P* N_2	α CO_2/CH_4	α CO_2/N_2
$[C_2mim][C_1SO_4]$	111 ± 0.8	3.49 ± 0.07	1.59 ± 0.02	31.7 ± 0.9	69.4 ± 1.4
$[C_2mim][C_2SO_4]$	157 ± 0.1	7.38 ± 0.02	3.06 ± 0.01	21.2 ± 0.1	51.3 ± 0.2
$[C_2mim][SCN]$[c]	263 ± 0.6	12.1 ± 0.06	4.65 ± 0.15	21.8 ± 0.2	56.6 ± 1.9
$[C_2mim][N(CN)_2]$[c]	476 ± 0.8	20.7 ± 0.01	7.03 ± 0.05	23.0 ± 0.1	67.8 ± 0.6
$[C_2mim][C(CN)_3]$	667 ± 0.7	34.4 ± 0.07	11.7 ± 0.03	19.4 ± 0.1	57.0 ± 0.2
$[C_2mim][B(CN)_4]$	742 ± 1.4	39.0 ± 0.01	15.1 ± 0.06	19.1 ± 0.1	49.0 ± 0.3
$[C_2mim][C_1SO_4]_{0.5}[SCN]_{0.5}$	142 ± 2.8	6.88 ± 0.06	2.29 ± 0.11	20.6 ± 0.6	61.7 ± 4.2
$[C_2mim][C_1SO_4]_{0.5}[N(CN)_2]_{0.5}$	207 ± 0.4	8.57 ± 0.03	3.56 ± 0.02	24.1 ± 0.1	58.2 ± 0.4
$[C_2mim][C_1SO_4]_{0.5}[C(CN)_3]_{0.5}$	346 ± 0.1	18.5 ± 0.06	7.38 ± 0.02	18.7 ± 0.1	46.9 ± 0.1
$[C_2mim][C_1SO_4]_{0.5}[B(CN)_4]_{0.5}$	373 ± 1.7	18.3 ± 0.04	7.20 ± 0.03	20.3 ± 0.1	51.8 ± 0.5
$[C_2mim][SCN]_{0.5}[N(CN)_2]_{0.5}$	324 ± 0.4	14.7 ± 0.04	5.29 ± 0.04	22.1 ± 0.2	61.2 ± 0.5
$[C_2mim][SCN]_{0.5}[C(CN)_3]_{0.5}$	332 ± 0.9	16.2 ± 0.06	5.78 ± 0.02	20.5 ± 0.1	57.4 ± 0.3
$[C_2mim][SCN]_{0.5}[B(CN)_4]_{0.5}$	445 ± 0.6	23.0 ± 0.03	8.71 ± 0.03	19.4 ± 0.1	51.1 ± 0.2

[a] Barrer (1 Barrer = 10^{-10} cm^3(STP)cm cm^{-2} s^{-1} $cmHg^{-1}$)

[b] The listed uncertainties represent the standard deviations, based on three experiments.

[c] Values taken from Tomé *et al*.[77]

The Robeson plots show that CO_2/CH_4 is a less favorable separation than CO_2/N_2 in SILMs combining either the pure ILs or their binary mixtures. Figure 8(a) indicates that the performances obtained for CO_2/CH_4 separation are bellow the upper bound, close to those available in the literature for other SILMs. Regarding the CO_2/N_2 separation, Figure 8(b) shows that the CO_2/N_2 separation performance of the $[C_2mim][N(CN)_2]$, $[C_2mim][C(CN)_3]$, and $[C_2mim][B(CN)_4]$-based SILMs are above the upper bound. These results are in agreement with other recently published studies on pure SILMs, where the use of ILs with cyano-containing anions leads to high CO_2/N_2 separation performances.[49, 52, 56]

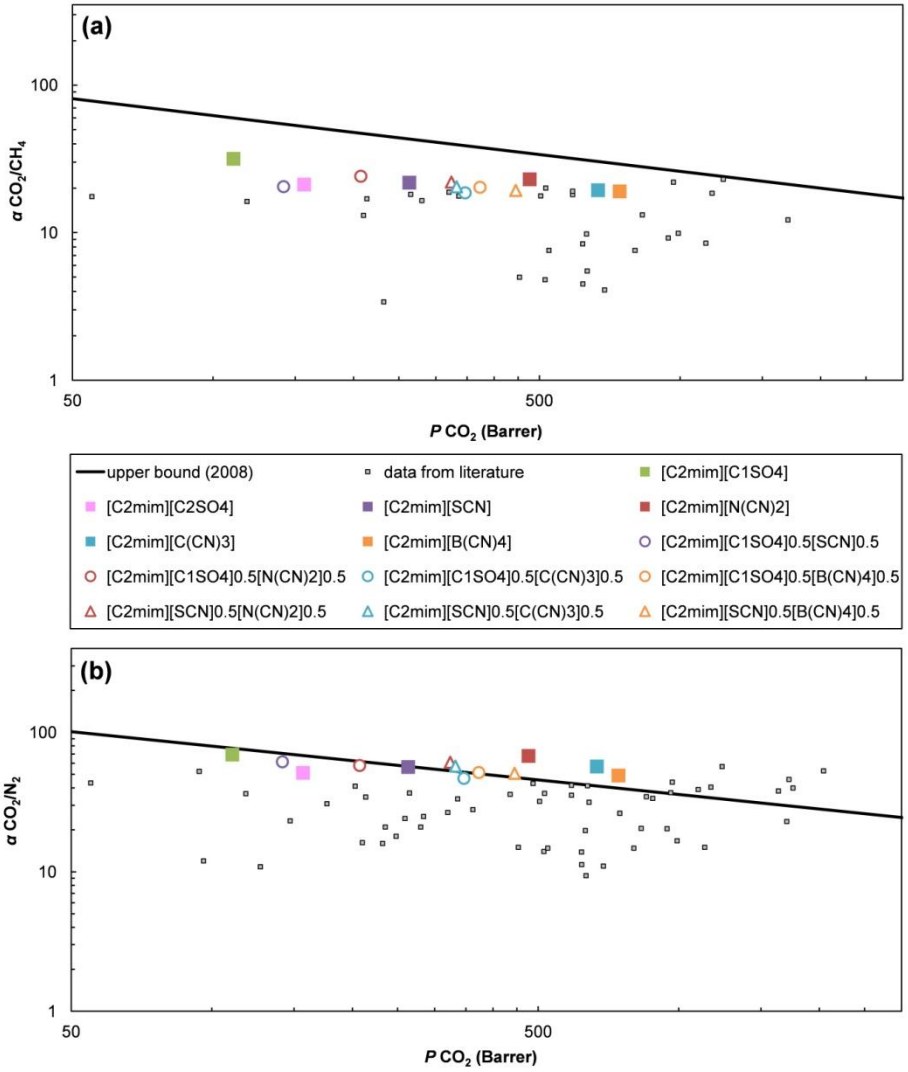

Figure 8| CO_2 separation performance of the studied SILMs potted on (a) CO_2/CH_4 and (b) CO_2/N_2 Robeson plots. Experimental error is within the data points. Data are plotted on a lo-log scale and the upper bound for each gas pair is adapted from Robeson.[89] Literature data reported for other supported ionic liquid membranes are also plotted in (a)[44, 62, 63, 70, 71, 77] and (b).[44, 52, 55, 56, 62-65, 68, 70, 71, 77] The values of $[C_2mim][SCN]$ and $[C_2mim][N(CN)_2]$-based SILMs were taken from Tomé *et al*.[77]

Although the pure ILs combining sulfate anions have lower CO_2 permeabilities than those of cyano-based ILs (Table 3), their CO_2/N_2 separation performances are also considerably good, in particular the $[C_2mim][C_1SO_4]$ SILM

achieved the upper bound (Figure 8(b)). Furthermore, Figure 8(a) and Figure 8(b) clearly show that the CO_2 separation performance of SILMs as a function of the permeability can be fine-tune by mixing ILs containing sulfate and cyano anions. For instance, mixtures of $[C_2mim][C_1SO_4]$ with ILs containing cyano-functionalized anions cause a shift of the separation performances results along the *x*-axis without significantly changing the CO_2/CH_4 and CO_2/N_2 permselectivities. Consequently, the studied supported IL mixtures membranes do not present the traditionally tradeoff between permselectivity and permeability usually observed for polymeric membranes,[89] where highly permeable membranes tend to exhibit less permselectivity and *vice-versa*. What is more, all the SILMs prepared with IL mixtures exceed or fall on the CO_2/N_2 upper bound, indicating that the IL mixtures proposed in this work are potential candidates as liquid phases for CO_2 separation.

5. Conclusions

In this work, new IL mixtures containing sulfate and/or cyano-functionalized anions are proposed as liquid phases in SILM configurations for CO_2 separation. The CO_2, CH_4, and N_2 permeation properties of these ILs mixtures were measured and the results show that is possible to use ionic liquid mixtures to design engineered CO_2 separation membranes with tailored gas permeation properties. Cyano-functionalized anions have a great impact on the gas permeation properties of SILMs. Depending on the number of cyano groups existing in the anion that is mixed, different gas permeabilities, diffusivities and solubilities can be obtained.

Overall, it was concluded that gas permeabilities through the SILMs are not entirely controlled by their gas diffusivities and respective IL viscosities. They are also linked to their respective CO_2 solubilities. Both the Camper Model and the Universal Model provide good descriptions of CO_2/N_2 and CO_2/CH_4 solubility

selectivity behavior for most of the pure ILs and also for binary IL mixtures containing the $[B(CN)_4]^-$ anion. However, deviations from both models were obtained for IL mixtures containing the $[N(CN)_2]^-$ or the $[C(CN)_3]^-$ anions, meaning that the IL molar volume as a single parameter cannot fully describe the solubility selectivity of those IL mixtures. Remarkably, the SILMs prepared with IL mixtures exceeded or achieved the upper bound of CO_2/N_2 separation, which makes them highly promising liquid phases in separation technologies for CO_2 low-pressure post-combustion processes. In conclusion, the results obtained in this study clearly claim that ionic liquid mixtures can be a powerful strategy for designing engineered membrane materials, since they offer a clear pathway to fine-tune their gas permeation properties as well as their CO_2 separation performances.

6. Acknowledgements

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7. Supplementary Information

7.1. Density

Densities of the pure ILs and their mixtures were measured in the temperature range from 293.15 K to 353.15 K and are reported in Table S1 and S2, and illustrated in Figure S1 and S2, respectively. Additionally, a comparison of these results with literature values is shown in Table S3. When comparing the experimental results obtained in this work with those published in the literature for the same pure ILs, it can be observed that they are consistent with each other, with the exception of the pure $[C_2mim][C_1SO_4]$, in which deviations of 0.31% for density and 16.1% for viscosity values were observed. These differences can be attributed to the content of water in the IL. However, a direct comparison cannot be made since some of the authors do not report the quantity of water in their samples.

The density decreases linearly with temperature, for all pure ILs and their mixtures, in the whole temperature range studied. The linear Equation (S1) was used to correlate the temperature dependence of the density:

$$\rho = a + b\,(T) \tag{S1}$$

where ρ corresponds to density (g cm^{-3}), T is the temperature (K) and a and b are the fitting parameters. The a and b values, derived from the equation (S1), obtained for all the studied samples are presented in Table S4.

The molar volumes (V_m) of the pure ILs and their mixtures are presented in Table S5 and S6, respectively. The excess molar volume (V^E) of the IL mixtures was calculated by Equation (S2):

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho_M} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \tag{S2}$$

where ρ corresponds to the density (g cm^{-3}), x is the mole fraction and the M corresponds to the molar mass (g mol^{-1}). The subscript *1* and *2* refer to the two pure ILs and the subscript M denotes the IL mixture. The calculated excess molar volumes are listed in Table S7 and depicted in Figure S3 for 293.15 K.

As expected, Figure S1 and Figure S2 show that the density values of the mixtures are in between those of the pure ILs. The density values can be grouped into two distinct groups: the sulfate-based ILs (values from 1.2 to 1.3 g cm^{-3}) and the cyano-based ILs (values from 1.0 to 1.15 g cm^{-3}). The density values of pure ILs decrease with the increase in the alkyl chain length in the sulfate anion and with the increase in the number of cyano groups in the anion of the IL (Figure S1). Accordingly, at a fixed temperature, the densities of the pure ILs can be ranked according to the following anion order: $[C_1SO_4]^-$ > $[C_2SO_4]^-$ > $[SCN]^-$ > $[N(CN)_2]^-$ > $[C(CN)_3]^-$ > $[B(CN)_4]^-$.

The excess molar volumes (V^E) are the result of contributions from several effects, namely: chemical, physical and structural modifications. Physical contributions originate positive V^E values, which are non-specific interactions between the real species present in the mixture.[6] Negative V^E values is a result of chemical contributions (charge-transfer type forces, changes in hydrogen bonding equilibrium or electrostatic interactions) or structural contributions (geometrical fitting or changes of free volume).[90] The V^E obtained for all the studied mixtures at different temperatures present positive values, with the exception of those obtained for the $[C_2mim][C_1SO_4]_{0.5}[N(CN)_2]_{0.5}$ mixture, that present a negative V^E in the whole range temperature, and for the $[C_2mim][SCN]_{0.5}[N(CN)_2]_{0.5}$ mixture that presented a negative V^E values for higher temperatures (from 343.15 K to 353.15 K).

Table S1| Measured densities, ρ (g cm^{-3}), of the pure ionic liquids studied in this work.

T (K)	$[C_2mim][C_1SO_4]$	$[C_2mim][C_2SO_4]$	$[C_2mim][SCN]$*	$[C_2mim][N(CN)_2]$*	$[C_2mim][C(CN)_3]$	$[C_2mim][B(CN)_4]$
293.15	1.294	1.241	1.119	1.106	1.085	1.040
298.15	1.291	1.237	1.116	1.103	1.081	1.036
303.15	1.287	1.234	1.113	1.099	1.077	1.032
308.15	1.284	1.231	1.110	1.096	1.074	1.029
313.15	1.281	1.227	1.107	1.093	1.070	1.025
318.15	1.278	1.224	1.104	1.090	1.067	1.021
323.15	1.274	1.221	1.101	1.086	1.064	1.017
328.15	1.271	1.218	1.098	1.083	1.060	1.013
333.15	1.268	1.214	1.095	1.080	1.057	1.010
338.15	1.265	1.211	1.092	1.077	1.054	1.006
343.15	1.261	1.208	1.089	1.074	1.050	1.002
348.15	1.258	1.205	—	—	1.047	0.999
353.15	1.255	1.201	—	—	1.043	0.995

*Values taken from Tomé *et al*.[77]

Table S2| Measured densities, ρ ($g \cdot cm^{-3}$), of the ionic liquid mixtures studied in this work.

T (K)	$[C_2mim][C_1SO_4]_{0.5}[SCN]_{0.5}$	$[C_2mim][C_1SO_4]_{0.5}[N(CN)_2]_{0.5}$	$[C_2mim][C_1SO_4]_{0.5}[C(CN)_3]_{0.5}$	$[C_2mim][C_1SO_4]_{0.5}[B(CN)_4]_{0.5}$	$[C_2mim][SCN]_{0.5}[N(CN)_2]_{0.5}$	$[C_2mim][SCN]_{0.5}[C(CN)_3]_{0.5}$	$[C_2mim][SCN]_{0.5}[B(CN)_4]_{0.5}$
293.15	1.211	1.203	1.179	1.144	1.112	1.099	1.070
298.15	1.208	1.200	1.176	1.140	1.108	1.096	1.067
303.15	1.205	1.196	1.172	1.137	1.105	1.092	1.063
308.15	1.201	1.193	1.169	1.133	1.102	1.089	1.060
313.15	1.198	1.190	1.165	1.129	1.099	1.086	1.056
318.15	1.195	1.186	1.162	1.126	1.096	1.083	1.053
323.15	1.192	1.183	1.159	1.122	1.093	1.080	1.049
328.15	1.189	1.180	1.155	1.119	1.090	1.076	1.046
333.15	1.186	1.177	1.152	1.115	1.087	1.073	1.042
338.15	1.183	1.174	1.149	1.111	1.084	1.070	1.039
343.15	1.180	1.170	1.145	1.108	1.081	1.067	1.036
348.15	1.177	1.167	1.142	1.104	1.078	1.064	1.032
353.15	1.174	1.164	1.139	1.101	1.075	1.060	1.029

Table S3| Comparison of density (ρ) and viscosity (η) values of the pure ionic liquids measured in this work with those from literature at 298.15 K.

Ionic liquids	ρ (g cm^{-3})		η (mPa s)	
	This Work	Literature	This Work	Literature
$[C_2mim][C_1SO_4]$	1.291	1.287 [91]	100.021	83.885 [91]
$[C_2mim][C_2SO_4]$	1.237	1.237 [92]	92.677	95.90 [92]
$[C_2mim][C(CN)_3]$	1.081	1.081 [93]	14.187	14.610 [79]
$[C_2mim][B(CN)_4]$	1.036	1.036 [79]	17.793	18.565 [79]

Table S4| Fitted parameters Equation (S1) for the studied ILs and their mixtures.

Ionic Liquids	b x 10^{-4}	a	r^2
$[C_2mim][C_1SO_4]$	-6.52	1.485	0.9995
$[C_2mim][C_2SO_4]$	-6.55	1.433	0.9994
$[C_2mim]$ [SCN]	-6.00	1.295	1.0000
$[C_2mim][N(CN)_2]$	-6.44	1.295	0.9992
$[C_2mim][C(CN)_3]$	-6.85	1.485	0.9995
$[C_2mim][B(CN)_4]$	-7.49	1.260	0.9996
$[C_2mim][C_1SO_4]_{0.5}[SCN]_{0.5}$	-6.16	1.391	0.9994
$[C_2mim][C_1SO_4]_{0.5}[N(CN)_2]_{0.5}$	-6.51	1.394	0.9994
$[C_2mim][C_1SO_4]_{0.5}[C(CN)_3]_{0.5}$	-6.71	1.376	0.9995
$[C_2mim][C_1SO_4]_{0.5}[B(CN)_4]_{0.5}$	-7.20	1.355	0.9996
$[C_2mim][SCN]_{0.5}[N(CN)_2]_{0.5}$	-6.07	1.289	0.9996
$[C_2mim][SCN]_{0.5}[C(CN)_3]_{0.5}$	-6.42	1.287	0.9994
$[C_2mim][SCN]_{0.5}[B(CN)_4]_{0.5}$	-6.89	1.272	0.9995

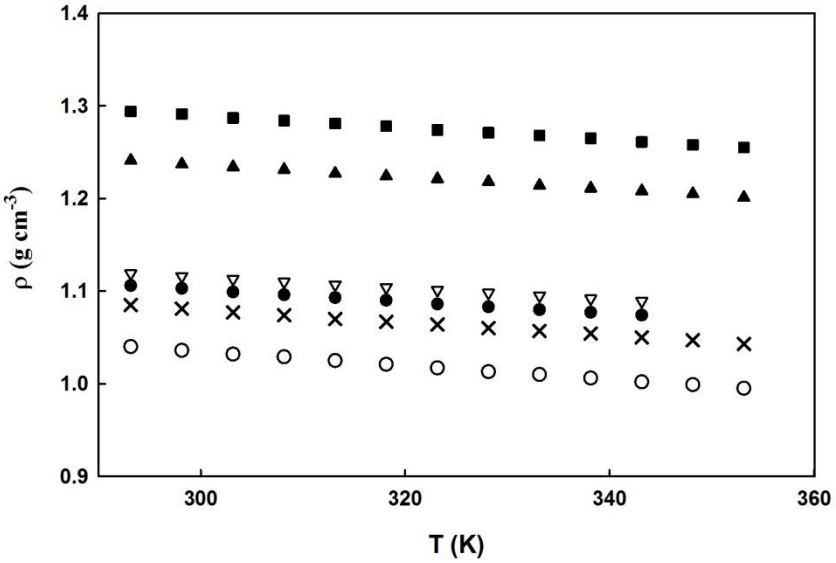

Figure S1| Densities (ρ) of the pure ionic liquids measured in this work as a function of temperature (T): $[C_2mim][C_1SO_4]$ (■), $[C_2mim][C_2SO_4]$ (▲), $[C_2mim][SCN]$ (▽), $[C_2mim][N(CN)_2]$ (●), $[C_2mim][C(CN)_3]$ (✕), $[C_2mim][B(CN)_4]$ (○).

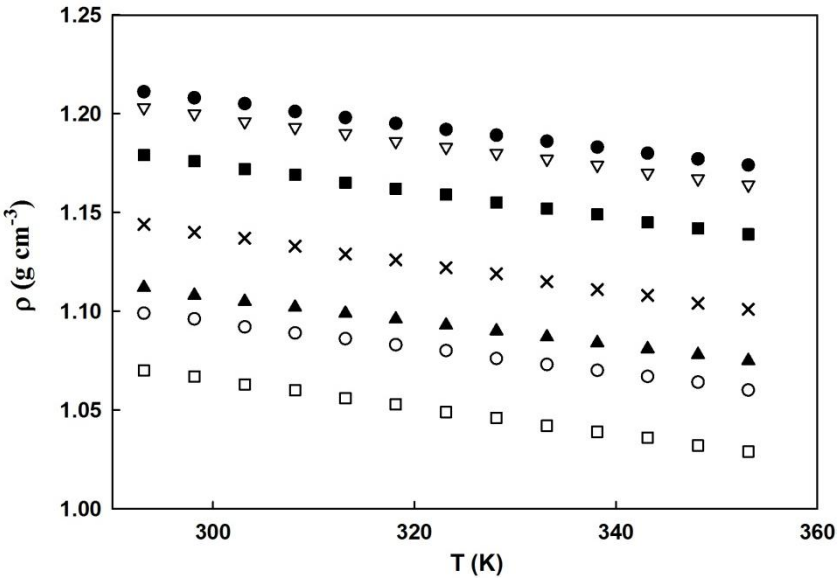

Figure S2| Densities (ρ) of the ionic liquid mixtures measured in this work as a function of temperature (T): $[C_2MIM][C_1SO_4]_{0.5}[SCN]_{0.5}$ (●), $[C_2MIM][C_1SO_4]_{0.5}[DCA]_{0.5}$ (▽), $[C_2MIM][C_1SO_4]_{0.5}[C(CN)_3]_{0.5}$ (■), $[C_2MIM][C_1SO_4]_{0.5}[B(CN)_4]_{0.5}$ (✕), $[C_2MIM][SCN]_{0.5}[DCA]_{0.5}$ (▲), $[C_2MIM][SCN]_{0.5}[C(CN)_3]_{0.5}$ (○), $[C_2MIM][SCN]_{0.5}[B(CN)_4]_{0.5}$ (□).

Table S5| Molar volumes, V_m ($cm^3\ mol^{-1}$), of the pure ionic liquids studied in this work.

T (K)	$[C_2mim][C_1SO_4]$	$[C_2mim][C_2SO_4]$	$[C_2mim][SCN]$*	$[C_2mim][N(CN)_2]$*	$[C_2mim][C(CN)_3]$	$[C_2mim][B(CN)_4]$
293.15	171.62	190.26	151.24	160.24	185.42	226.89
298.15	172.07	190.79	151.66	160.73	186.04	227.76
303.15	172.51	191.31	152.08	161.22	186.64	228.63
308.15	172.95	191.83	152.50	161.70	187.26	229.49
313.15	173.38	192.35	152.91	162.19	187.87	230.33
318.15	173.82	192.85	153.33	162.65	188.46	231.20
323.15	174.27	193.37	153.74	163.13	189.06	232.07
328.15	174.71	193.89	154.15	163.61	189.67	232.94
333.15	175.16	194.41	154.55	164.10	190.27	233.80
338.15	175.61	194.94	154.96	164.59	190.88	234.67
343.15	176.07	195.46	155.38	165.08	191.49	235.54
348.15	176.53	196.00	—	—	192.11	236.35
353.15	177.00	196.55	—	—	192.74	237.25

*Values taken from Tomé *et al.*[77]

Table S6| Molar volumes, V_m ($cm^3\ mol^{-1}$), of the pure ionic liquid mixtures studied in this work.

T (K)	$[C_2mim][C_1SO_4]_{0.5}[SCN]_{0.5}$	$[C_2mim][C_1SO_4]_{0.5}[N(CN)_2]_{0.5}$	$[C_2mim][C_1SO_4]_{0.5}[C(CN)_3]_{0.5}$	$[C_2mim][C_1SO_4]_{0.5}[B(CN)_4]_{0.5}$	$[C_2mim][SCN]_{0.5}[N(CN)_2]_{0.5}$	$[C_2mim][SCN]_{0.5}[C(CN)_3]_{0.5}$	$[C_2mim][SCN]_{0.5}[B(CN)_4]_{0.5}$
293.15	161.55	165.94	179.41	200.24	155.85	168.48	189.34
298.15	161.99	166.41	179.95	200.89	156.31	169.01	189.99
303.15	162.42	166.88	180.49	201.55	156.76	169.52	190.62
308.15	162.85	167.34	181.02	202.21	157.21	170.03	191.26
313.15	163.26	167.81	181.56	202.85	157.66	170.54	191.89
318.15	163.69	168.27	182.10	203.48	158.10	171.04	192.51
323.15	164.12	168.74	182.63	204.14	158.54	171.54	193.15
328.15	164.55	169.18	183.14	204.79	158.98	172.04	193.78
333.15	164.98	169.64	183.67	205.45	159.42	172.54	194.43
338.15	165.41	170.10	184.21	206.10	159.86	173.06	195.06
343.15	165.83	170.56	184.74	206.76	160.30	173.58	195.70
348.15	166.26	171.04	185.28	207.42	160.75	174.10	196.35
353.15	166.71	171.50	185.82	208.08	161.21	174.62	196.99

Table S7| Excess molar volumes, V^E ($cm^3\ mol^{-1}$), of the ionic liquid mixtures studied in this work.

T (K)	$[C_2mim][C_1SO_4]_{0.5}[SCN]_{0.5}$	$[C_2mim][C_1SO_4]_{0.5}[N(CN)_2]_{0.5}$	$[C_2mim][C_1SO_4]_{0.5}[C(CN)_3]_{0.5}$	$[C_2mim][C_1SO_4]_{0.5}[B(CN)_4]_{0.5}$	$[C_2mim][SCN]_{0.5}[N(CN)_2]_{0.5}$	$[C_2mim][SCN]_{0.5}[C(CN)_3]_{0.5}$	$[C_2mim][SCN]_{0.5}[B(CN)_4]_{0.5}$
293.15	0.1451	-0.0791	0.8889	0.9872	0.0487	0.1800	0.2998
298.15	0.1483	-0.0779	0.8954	0.9790	0.0530	0.1842	0.3036
303.15	0.1560	-0.0697	0.9121	0.9771	0.0548	0.1883	0.2963
308.15	0.1707	-0.0705	0.9187	0.9877	0.0683	0.1935	0.3127
313.15	0.1627	-0.0552	0.9373	0.9969	0.0705	0.1925	0.3184
318.15	0.1569	-0.0560	0.9558	0.9697	0.0678	0.1926	0.2945
323.15	0.1625	-0.0543	0.9662	0.9740	0.0603	0.1815	0.2893
328.15	0.1636	-0.0717	0.9525	0.9682	0.0478	0.1779	0.2863
333.15	0.1624	-0.0848	0.9553	0.9675	0.0373	0.1719	0.2908
338.15	0.1565	-0.0980	0.9634	0.9590	0.0220	0.1773	0.2797
343.15	0.1412	-0.1240	0.9584	0.9596	-0.0064	0.1796	0.2761
348.15	0.1208	-0.1454	0.9557	0.9791	-0.0446	0.1639	0.2944
353.15	0.1002	-0.1661	0.9483	0.9504	-0.0625	0.1486	0.2548

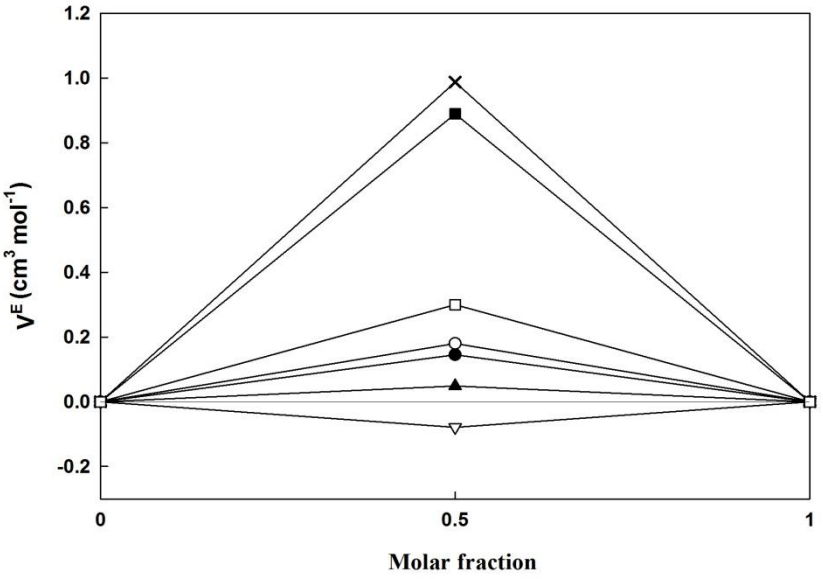

Figure S4| Excess molar volumes of the studied ionic liquid mixtures at 293.15 K: $[C_2MIM][C_1SO_4]_{0.5}[SCN]_{0.5}$ (●), $[C_2mim][C_1SO_4]_{0.5}[N(CN)_2]_{0.5}$ (▽), $[C_2mim][C_1SO_4]_{0.5}[C(CN)_3]_{0.5}$ (■), $[C_2MIM][C_1SO_4]_{0.5}[B(CN)_4]_{0.5}$ (✕), $[C_2MIM][SCN]_{0.5}[N(CN)_2]_{0.5}$ (▲), $[C_2mim][SCN]_{0.5}$ $[C(CN)_3]_{0.5}$ (○), $[C_2mim][SCN]_{0.5}[B(CN)_4]_{0.5}$ (□).

7.2. Viscosity

Viscosity values for the pure ILs and their mixtures, in a temperature range from 293.15 K to 353.15 K, are listed in Table S8 and Table S9 and depicted in Figure S4 and Figure S5, respectively. The viscosity deviations ($\Delta\eta$) for the IL mixtures were calculated using Equation (S3).

$$\Delta \ln(\eta) = \ln(\eta_M) - [x_1 \ln(\eta_1) + (1 - x_1) \ln(\eta_2)] \quad \text{(S3)}$$

where η corresponds to viscosity (mPa s) and x is the mole fraction. The subscript *1* and *2* correspond to the two pure ILs and the subscript *M* denotes the IL mixture. The calculated viscosity deviations values are presented in Table S10. The viscosity deviations for the studied mixtures are represented in Figure S6, at 293.15 K.

For all pure ILs and also their mixtures, the viscosity decreases with temperature. This behavior was correlated using a logarithmic equation based on Arrhenius model, described by the Equation (S4):

$$\ln(\eta) = \ln(a) - \frac{E_a}{RT} \quad \text{(S4)}$$

where η is the viscosity (mPa s), E_a is the activation energy (kJ mol^{-1}), R is the ideal gas constant and T is the temperature (K). The fitted parameters are listed in Table S11.

As observed for density, the viscosity of the IL mixtures display intermediate values between those of the pure ILs. Accordingly, at a fixed temperature, the viscosity of pure ILs can be ordered by the following order of the anions: $[C_1SO_4]^-$ > $[C_2SO_4]^-$ > $[SCN]^-$ > $[B(CN)_4]^-$ > $[N(CN)_2]^-$> $[C(CN)_3]^-$. Furthermore, the viscosities of the sulfate-based ILs and the cyano-based ILs are very different from each other, meaning that, as density, this property is directly related to the chemical structure of the anion.

Both negative and positive viscosity deviations were found for the IL mixtures studied in this work. As it can be seen from Table S10, all the mixtures studied show negative values in the entire range of temperatures, with the exception of the following mixtures: $[C_2mim][C_1SO_4]_{0.5}[SCN]_{0.5}$, $[C_2mim][C_1SO_4]_{0.5}[N(CN)_2]_{0.5}$ and $[C_2MIM][C_1SO_4]_{0.5}[B(CN)_4]_{0.5,}$ which presented positive viscosity deviations values at some temperatures. Nevertheless, the deviations from ideality are very small. In terms of activation energies, it is interesting to observe that the pure ILs containing sulfate anions, namely $[C_2mim][C_1SO_4]$ and $[C_2mim][C_2SO_4]$, show a more pronounce temperature dependence viscosities compared to the cyano-based ILs, which is illustrated by its larger E_a value.

The use of Equation (S4) to describe the temperature behaviour of viscosity allows the discussion of the energy barrier of a fluid to shear stress, E_a values. The higher the E_a, the more difficult is the ions to move past each other. This can be a direct consequence of the size or entanglement of the ions and/or the presence of stronger interactions within the fluid. The activation energies (E_a) of pure ILs can be interpreted as follows: the pure ILs composed by anions having the sulfate groups exhibited the highest E_a, approximately 30 kJ mol^{-1}; and the pure ILs combining cyano groups in their anion structure present values of E_a of about 20 kJ mol^{-1}.

Table S8| Measured viscosities, η (mPa s), of the pure ionic liquids studied in this work.

T (K)	$[C_2mim][C_1SO_4]$	$[C_2mim][C_2SO_4]$	$[C_2mim][SCN]$*	$[C_2mim][N(CN)_2]$*	$[C_2mim][C(CN)_3]$	$[C_2mim][B(CN)_4]$
293.15	127.523	119.987	27.846	17.947	16.624	21.434
298.15	100.021	92.677	23.431	15.426	14.187	17.793
303.15	79.863	73.015	19.937	13.366	12.177	14.933
308.15	64.789	58.563	17.146	11.696	10.578	12.696
313.15	53.474	47.866	14.900	10.323	9.024	10.668
318.15	44.430	39.451	13.058	9.177	8.202	9.490
323.15	37.443	33.041	11.538	8.222	7.314	8.324
328.15	31.902	27.975	10.269	7.410	6.563	7.359
333.15	27.520	23.993	9.200	6.712	5.719	6.354
338.15	23.805	20.676	8.289	6.115	5.379	5.883
343.15	20.794	18.005	7.511	5.597	4.910	5.305
348.15	18.305	15.797	—	—	4.501	4.814
353.15	16.146	13.996	—	—	3.980	4.230

*Values taken from Tomé *et al.*[77]

Table S9| Measured viscosities, η (mPa s), of the ionic liquid mixtures studied in this work.

T (K)	$[C_2mim][C_1SO_4]_{0.5}[SCN]_{0.5}$	$[C_2mim][C_1SO_4]_{0.5}[N(CN)_2]_{0.5}$	$[C_2mim][C_1SO_4]_{0.5}[C(CN)_3]_{0.5}$	$[C_2mim][C_1SO_4]_{0.5}[B(CN)_4]_{0.5}$	$[C_2mim][SCN]_{0.5}[N(CN)_2]_{0.5}$	$[C_2mim][SCN]_{0.5}[C(CN)_3]_{0.5}$	$[C_2mim][SCN]_{0.5}[B(CN)_4]_{0.5}$
293.15	60.380	49.200	41.022	53.726	21.287	20.711	23.233
298.15	48.805	40.105	33.341	42.771	18.233	17.560	19.442
303.15	40.075	33.151	27.508	34.690	15.714	15.007	16.435
308.15	33.365	27.778	23.034	28.596	13.678	12.970	14.068
313.15	28.097	23.429	19.346	23.801	11.764	11.070	11.913
318.15	23.981	20.187	16.747	20.377	10.644	9.977	10.607
323.15	20.651	17.491	14.513	17.326	9.494	8.858	9.331
328.15	17.939	15.283	12.688	14.994	8.528	7.925	8.251
333.15	15.697	13.402	11.063	13.026	7.507	6.933	7.158
338.15	13.886	11.943	9.937	11.525	6.999	6.460	6.602
343.15	12.347	10.669	8.885	10.226	6.391	5.880	5.953
348.15	11.045	9.588	7.996	9.135	5.863	5.378	5.404
353.15	9.909	8.614	7.150	8.144	5.252	4.784	4.765

Table S10| Viscosity deviations, $\Delta\eta$ (mPa s), of the ionic liquid mixtures studied in this work.

T (K)	$[C_2mim][C_1SO_4]_{0.5}[SCN]_{0.5}$	$[C_2mim][C_1SO_4]_{0.5}[N(CN)_2]_{0.5}$	$[C_2mim][C_1SO_4]_{0.5}[C(CN)_3]_{0.5}$	$[C_2mim][C_1SO_4]_{0.5}[B(CN)_4]_{0.5}$	$[C_2mim][SCN]_{0.5}[N(CN)_2]_{0.5}$	$[C_2mim][SCN]_{0.5}[C(CN)_3]_{0.5}$	$[C_2mim][SCN]_{0.5}[B(CN)_4]_{0.5}$
293.15	0.0102	0.0557	-0.1155	0.0273	-0.0242	-0.0411	-0.0532
298.15	0.0037	0.0439	-0.1220	0.0138	-0.0232	-0.0420	-0.0534
303.15	-0.0008	0.0356	-0.1255	0.0045	-0.0221	-0.0426	-0.0538
308.15	-0.0044	0.0282	-0.1280	-0.0030	-0.0210	-0.0431	-0.0531
313.15	-0.0027	0.0270	-0.1270	-0.0035	-0.0211	-0.0445	-0.0548
318.15	-0.0110	0.0150	-0.1309	-0.0077	-0.0194	-0.0432	-0.0549
323.15	-0.0136	0.0104	-0.1313	-0.0188	-0.0192	-0.0436	-0.0562
328.15	-0.0164	0.0059	-0.1314	-0.0216	-0.0182	-0.0427	-0.0597
333.15	-0.0125	0.0117	-0.1257	-0.0150	-0.0189	-0.0441	-0.0647
338.15	-0.0203	-0.0017	-0.1299	-0.0265	-0.0172	-0.0417	-0.0649
343.15	-0.0212	-0.0039	-0.1286	-0.0267	-0.0163	-0.0414	-0.0677
348.15	-0.0228	-0.0066	-0.1268	-0.0273	-0.0161	-0.0410	-0.0699
353.15	-0.0152	0.0065	-0.1144	-0.0146	-0.0152	-0.0433	-0.0776

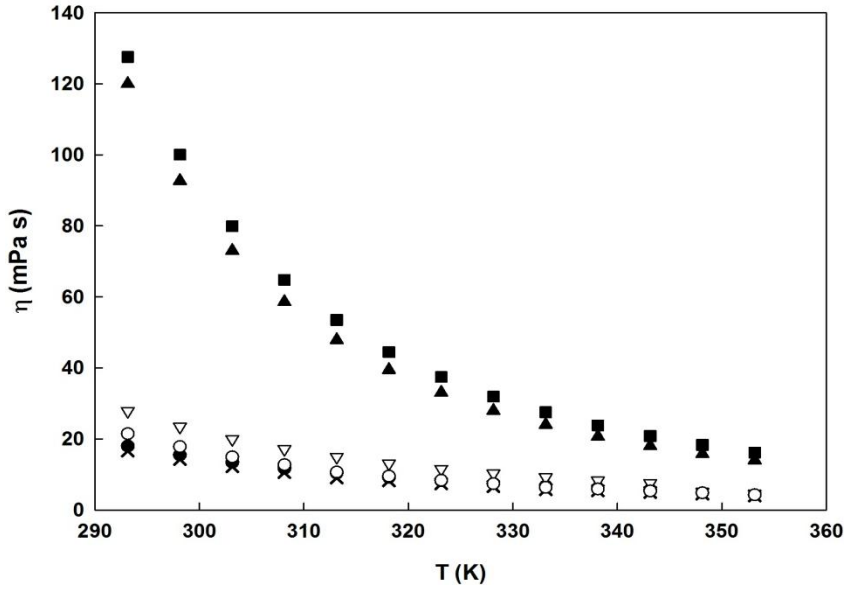

Figure S4| Measured viscosities of the pure ionic liquids studied in this work as a function of temperature (T): $[C_2mim][C_1SO_4]$ (■), $[C_2mim][C_2SO_4]$ (▲), $[C_2mim][SCN]$ (▽), $[C_2mim][N(CN)_2]$ (●), $[C_2mim][C(CN)_3]$ (✕) and $[C_2mim][B(CN)_4]$ (○).~

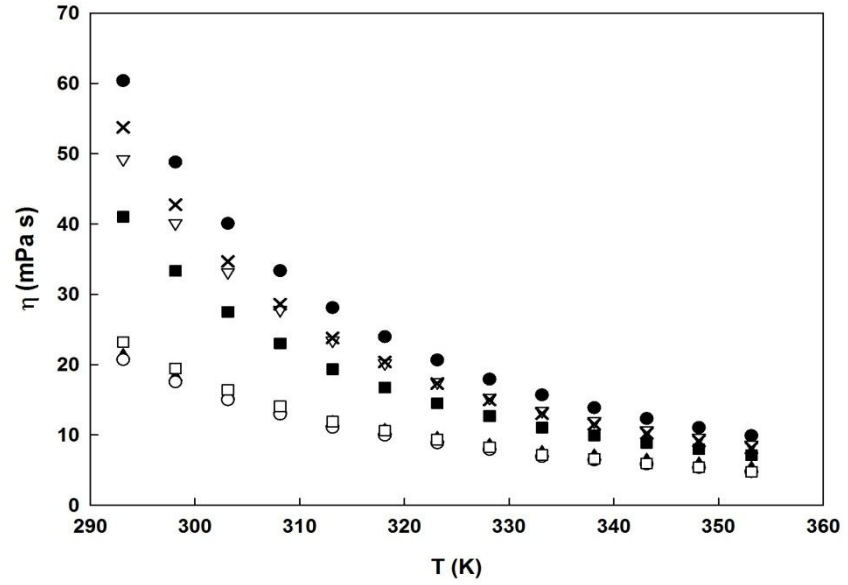

Figure S5| Measured viscosities of the ionic liquid mixtures studied in this work: $[C_2mim][C_1SO_4]_{0.5}[SCN]_{0.5}$ (●), $[C_2mim][C_1SO_4]_{0.5}[N(CN)_2]_{0.5}$ (▽), $[C_2mim][C_1SO_4]_{0.5}[C(CN)_3]_{0.5}$ (■), $[C_2mim][C_1SO_4]_{0.5}[B(CN)_4]_{0.5}$ (✕), $[C_2mim][SCN]_{0.5}[N(CN)_2]_{0.5}$ (▲), $[C_2mim][SCN]_{0.5}$ $[C(CN)_3]_{0.5}$ (○), $[C_2mim][SCN]_{0.5}[B(CN)_4]_{0.5}$ (□).

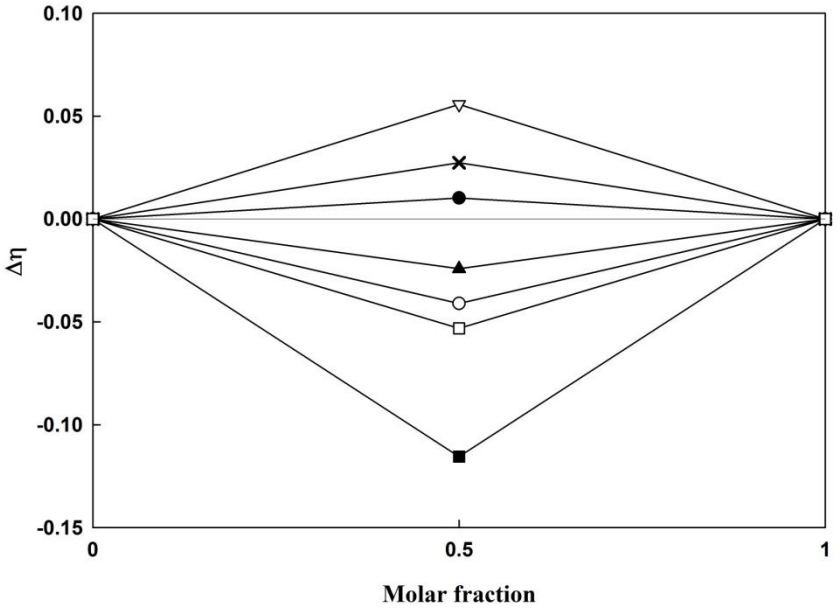

Figure S6| Viscosity deviations of the ionic liquid mixtures studied in this work at 293.15 K: $[C_2mim][C_1SO_4]_{0.5}[SCN]_{0.5}$ (●), $[C_2mim][C_1SO_4]_{0.5}[N(CN)_2]_{0.5}$ (▽), $[C_2mim][C_1SO_4]_{0.5}[C(CN)_3]_{0.5}$ (■), $[C_2mim][C_1SO_4]_{0.5}[B(CN)_4]_{0.5}$ (✕), $[C_2mim][SCN]_{0.5}[N(CN)_2]_{0.5}$ (▲), $[C_2mim][SCN]_{0.5}$ $[C(CN)_3]_{0.5}$ (○), $[C_2mim][SCN]_{0.5}[B(CN)_4]_{0.5}$ (□).

Table S11| Correlation parameters of Equation (S4).

Ionic Liquids	η_∞ x 10^{-3}	*-Ea* (KJ mol^{-1})	r^2
$[C_2mim][C_1SO_4]$	0.683	29.42	0.9972
$[C_2mim][C_2SO_4]$	0.388	30.62	0.9963
$[C_2mim]$ [SCN]	3.46	21.84	0.9981
$[C_2mim][N(CN)_2]$	6.02	19.43	0.9983
$[C_2mim][C(CN)_3]$	4.23	20.07	0.9967
$[C_2mim][B(CN)_4]$	1.74	22.83	0.9965
$[C_2mim]$ $[C_1SO_4]_{0.5}[SCN]_{0.5}$	1.47	25.74	0.9970
$[C_2mim][C_1SO_4]_{0.5}[N(CN)_2]_{0.5}$	1.77	24.80	0.9969
$[C_2mim][C_1SO_4]_{0.5}[C(CN)_3]_{0.5}$	1.48	24.79	0.9964
$[C_2mim][C_1SO_4]_{0.5}[B(CN)_4]_{0.5}$	0.841	26.79	0.9962
$[C_2mim][SCN]_{0.5}[N(CN)_2]_{0.5}$	6.15	19.77	0.9973
$[C_2mim][SCN]_{0.5}[C(CN)_3]_{0.5}$	4.16	20.64	0.9969
$[C_2mim][SCN]_{0.5}[B(CN)_4]_{0.5}$	2.32	22.34	0.9975

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Chapter 4

Polymeric ionic liquid membranes: influence of polycation variation

Adapted from: **L.C. Tomé,** A.S.L. Gouveia, C.S.R. Freire, D. Mecerreyes I.M. Marrucho, Polymeric ionic liquid-based membranes: influence of polycation variation on gas transport and CO_2 separation performance, *submitted manuscript,* 2014.

The author was involved in all the experimental work, as well as on the discussion and preparation of the manuscript. The preparation of membranes was performed by A.S.L. Gouveia.

1. Abstract

This work evaluates the CO_2, CH_4, and N_2 permeation properties of five novel composite membranes based on polymeric ionic liquids (PILs) having different cation pendant units, namely imidazolium, pyridinium, pyrrolidinium, ammonium and cholinium, combined with the same counter-anion ($[NTf_2]^-$). The results show that the CO_2 permeability in the composite membranes is related to their respective CO_2 diffusivities, which are dependent on the PIL polycation nature. The composite membranes of the PILs containing different polycations and 10 wt% of free ionic liquid (IL) with similar structures to each PIL monomeric unit have CO_2 permeabilities between 3.66 and 20.4 Barrer, while they exhibit permselectivities ranging from 28.3 to 43.0 for CO_2/CH_4 and from 25.8 to 34.7 for CO_2/N_2. The best CO_2 permselectivities were obtained when tetra-alkyl ammonium-based PILs (pyrrolidinium, ammonium and cholinium) are used rather than imidazolium or pyridinium. Also, the results of this work indicate that the polycation backbones of PILs can also play a significant role in the design of PIL–IL membranes with the finest gas permeation properties and improved CO_2 separation performances.

2. Introduction

The efficient separation of carbon dioxide from other light gases is a key chemical engineering and environmental challenge which has been extensively researched in recent years.[1] In particular, CO_2/CH_4 separation is of paramount importance in natural gas purification since CO_2 is a contaminant that not only reduces the heating value of methane gas as a fuel source but also causes corrosion in pipelines.[2-4] Additionally, the imminent climate change issues and environmental risks, due to increasing concentrations of anthropogenic CO_2, have recently

highlighted the importance of carbon dioxide recovery from flue gas (CO_2/N_2 separation) produced by combustion of fossil fuels in electric power plants.[5, 6]

Different technologies, including absorption with amines, pressure swing adsorption using porous solids, cryogenic separation and membranes, have been proposed for CO_2 separation.[7-11] Although amines have advantages such as high reactivity and good absorption capacity allowing for highly efficient separation of CO_2 from the stream, their use is of environmental and economical concern owing to their corrosive nature, volatility, and in some cases toxicity.[7] Besides cryogenic distillation and pressure swing adsorption processes which require high amounts of energy and equipment costs, gas membrane separation technology present several advantages such as low energy consumption and operating costs, easy scale-up and incorporation into existing processes, and small foot print.[11-13] The major challenge in membrane operation, other than long operation term under different environmental conditions, is the need of having membranes with simultaneously high CO_2 permeability and selectivity.[13] Thus, industrial and academic research has been undertaken and currently the goal is to design novel materials with improved CO_2 separation performances in order to make membrane-based processes more competitive.

A quite recent approach for CO_2 separation makes use of ILs, a class of materials that offer a unique set of properties such as negligible vapor pressure, high thermal stability, low flammability, and high CO_2 solubility and selectivity over other light gases. As a chemical platform, their most attractive feature within the CO_2 separation context is perhaps the easy tailoring of their physical/chemical properties, as well as their CO_2 affinity.[14-18] Many researchers have exploited these properties using supported ionic liquid membrane (SILM) configurations,[19-27] in which the desired IL is immobilized into the pores of an inert polymer membrane by capillary forces. Nevertheless, SILMs stability is still an open issue and their operation is only possible at low pressures due to the risk of IL draining from the

support pores.[28] In order to circumvent this drawback, different approaches have been explored to prepare CO_2 separation membranes using ILs. For instance, polymer–IL composite membranes have been developed by blending ILs with poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP).[29-31] These membranes have shown good mechanical strength and favorable gas transport properties, but a limiting working pressure was also observed. Since the IL is entrapped in the tight spaces between the polymer chains, there are no chemical bonds tethering the IL to the polymer, and consequently high pressure differentials compress the membrane and cast out the IL. Alternatively, and considering that ILs present a unique platform for monomer design, the most promising way to take advantage of ILs for CO_2 separation, and simultaneously overcome the inherent disadvantages of the previous approaches, is to polymerize IL monomers and prepare polymeric ionic liquid-based membranes.[32]

Polymeric ionic liquids or poly(ionic liquid)s are a new generation of functional materials that comprise IL species connected through a polymeric backbone generating a macromolecular architecture.[33] The potential of PILs as CO_2 separation membranes was initially addressed in 2006 by Noble's group.[34] Neat PIL membranes with functionalized imidazolium cation units containing substituent groups such as *n*-alkyl,[35] oligo(ethylene glycol) or alkyl-terminated nitrile,[36] were fabricated by photo-initiated chain-addition polymerization and their gas permeation properties were studied. Whilst these membranes demonstrated good CO_2/CH_4 and CO_2/N_2 permselectivities, their CO_2 permeabilities and diffusivities were significantly lower than those observed in analogous SILMs.[28] Consequently, different strategies have been investigated to design PIL-based membranes with improved CO_2 permeability and selectivity, including the blending of free ILs with PILs to form homogeneous PIL–IL composites,[37-45] the synthesis of PIL copolymers to control segmental motion and chain packing for increasing gas permeability and mechanical stability of the

membranes,[46-49] and the incorporation of zeolites into PILs to prepare PIL–IL–zeolite mixed matrix membranes.[50, 51] Despite all the progresses and considering that the PIL-based CO_2 separation membranes tested so far comprise imidazolium-based PILs as polymer matrices,[35-40, 42-48] with the exception of our two recent studies where PIL with pyrrolidinium polycations were used,[41, 49] additional research is still required to complete understand the relationships between PIL chemical structures and gas permeation properties. Although valuable clues regarding the role of specific structural variations on the imidazolium cationic moieties of the polymeric backbone,[34-39] or the influence of using different anions,[40, 49, 52, 53] can be gathered from literature, the gas permeation properties of PIL-based membranes having different cation functionalities attached to their polycation backbones have not yet been studied.

In the present work, five novel membranes based on PILs containing the most important ionic liquid cations (imidazolium, pyridinium, pyrrolidinium, ammonium and cholinium) and the bis(trifluoromethylsulfonyl)imide ($[NTf_2]^-$) as counter-anion, were prepared by the solvent casting method and gas permeation experiments using CO_2, CH_4, and N_2 were performed in order to fully explore the influence of polycation functionality in the CO_2 separation performance of PIL-based membranes for natural gas purification and flue gas separation. The PILs used herein (Figure 1) were prepared in general via synthetic routes that consist on conventional free radical polymerization of the different prepared monomers with a thermal initiator followed by simple anion exchange reactions of the halides. The $[NTf_2]^-$ was selected as the PILs counter-anion due, not only to its inherent CO_2-phylic behavior and high thermal stability, but also to its relatively high commercial availability.

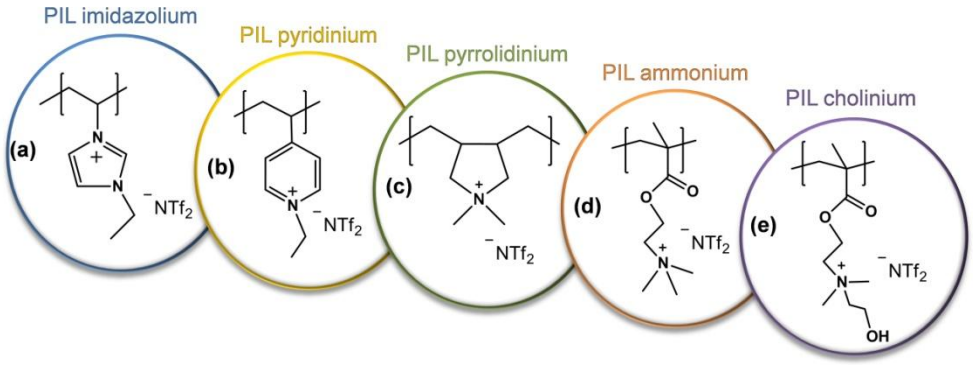

Figure 1| Chemical structures of the prepared polymeric ionic liquids (PILs): (a) poly([ViEtIm][NTf_2]), (b) poly([ViEtPy][NTf_2]), (c) poly([Pyr_{11}][NTf_2]) (d) poly([EMTMA][NTf_2]), (e) poly([EMCh][NTf_2]).

3. Experimental Section

3.1. Materials

Bromoethane (≥ 99%), 2-bromoethanol (95%), 1-vinylimidazole (≥ 99%), 4-vinylpyridine (95%), poly(diallyldimethylammonium) chloride solution (average Mw 400,000-500,000, 20 wt% in water), 2-(methacryloyloxy)ethyl trimethylammonium chloride solution (80 wt% in water), 2-(dimethylamino)ethyl methacrylate (98%), 2,2'-azobis (2-methylpropionamidine) dihydrochloride (AIBA, 97%), methanol (99.8%), acetonitrile (99.8%), acetone (99.8%) and ethyl acetate (99.8%) were purchased from Sigma-Aldrich. Lithium bis(trifluoromethylsulfonyl)imide salt ($LiNTf_2$, 99%) was supplied by IoLiTec GmbH. All the chemicals utilized as starting materials in the synthesis of monomers and polymers were used as received without further purification. The water was double distilled, passed through a reverse osmosis system and further treated with a Milli-Q plus 185 water purification equipment. CO_2, CH_4, and N_2 were supplied by Air Liquide and were of at least 99.99% purity.

IoLiTec GmbH provided 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C_2mim][NTf_2]) (99 wt% pure), 1-ethyl-3-

methylpyridinium bis(trifluoromethylsulfonyl)imide ([C_2mpy][NTf_2]) (99 wt% pure), 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([C_4mpyr][NTf_2]) (99 wt% pure), and butyltrimethylammonium bis(trifluoromethylsulfonyl)imide ([N_{4111}][NTf_2]) (99 wt% pure).

Also called as ethylcholinium bistriflamide, *N*-ethyl-*N,N*-dimethyl-*N*-(2-hydroxyethyl)ammonium bis(trifluoromethylsulfonyl)imide ([$N_{1122(OH)}$][NTf_2]) (purity of 99%) was synthesized in our lab according to previously described synthetic routes.[54]

In order to reduce the water and other volatile substances content, all the ionic liquid samples were dried under vacuum and subject to vigorous stirring at ≈ 333 K for at least 2 days immediately prior to use. No further purification of the purchased ionic liquids was carried out, but their purities were further evaluated by ^{1}H and ^{13}C RMN analysis and were found to be in accordance with the levels given by the supplier.

3.3. Synthesis of polymeric ionic liquids

Five polymeric ionic liquids (PILs) (Figure 1) containing different polycations, namely imidazolium, pyridinium, pyrrolidinium, ammonium and cholinium pendant units, and $[NTf_2]^-$ as counter-anion, were synthesized according to established literature procedures.[55-58] As it can be seen in Figure 2, depending on the target PILs different reaction schemes were used. Overall, polymerizable ionic liquid-based monomers containing the desired cation units combined with halide anions were synthesized and conventional free radical polymerization followed by simple anion exchange reaction were carried out in order to prepare the different polycations having $[NTf_2]^-$ as counter-anion. The chemical structures of the prepared PILs were confirmed by ^{1}H- and ^{13}C-NMR analysis (not shown).

Poly([ViEtIm][NTf$_2$]) (Figure 2(a)). The monomer 1-vinyl-3-ethyl-imidazolium bromide was prepared by mixing 10 g of 1-vinylimidazole (106.2 mmol), previously distillated, with 17.4 g of bromoethane (159.3 mmol). The mixture was then allowed to react at 318 K, in an oil bath for 16 hours with constant and vigorous stirring. After cooling down at 268 K overnight, the resulting white precipitate was washed several times with ethyl acetate, filtered and dissolved in methanol, which was then removed in a rotary evaporator. The product was dried in a vacuum oven at room temperature until constant weight was attained (yield: 76 %) and its purity was confirmed by ^{1}H-NMR.

Poly([ViEtIm][Br]) was then synthesized by conventional free radical polymerization in water. In a typical procedure, 15 g (73.9 mmol) of the prepared 1-vinyl-3-ethyl-imidazolium bromide were dissolved in 150 mL of distillated water in a round bottom flask. Then, an aqueous solution of the thermal radical initiator (0.075 g of AIBA and 2 mL of water) was added dropwise to the polymer solution and all the reactants were mixed by vigorous stirring and purged with dry nitrogen for 30 min, before the sealed flask was immersed in an oil bath at 338 K and kept for 3 hours. The amount of the AIBA initiator was 0.5 wt% of the monomer used. After cooling down to room temperature, the resulting aqueous solution was slowly dropwise added to an excess amount of acetone in order to precipitate the polymer, which was then filtered and dried under vacuum at 338 K until constant weight was attained (yield: 90%).

To prepare the poly([ViEtIm][NTf$_2$]), a simple anion exchange method was used, according to a procedure previously reported.[55] Briefly, the poly([ViEtIm][Br]) (8 g, 39.4 mmol) was dissolved in water (150 mL) and mixed by stirring for 30 min with an excess of an aqueous solution of LiNTf$_2$ (13.57 g, 47.3 mmol). Immediately after mixing, the formed polymer became hydrophobic and precipitated in the aqueous media as a result of the anion exchange reaction. The

obtained yellow solid was washed with an excess amount of water, filtered and dried in a vacuum oven at 338 K until constant weight was attained (yield: 87%).

Poly([ViEtPy][NTf$_2$]) (Figure 2(b)). First, bromoethane (15.5 g, 142.7 mmol) was added dropwise under vigorous stirring to 10 g of 4-vinylpyridine (95.1 mmol) in a 100 mL one neck round bottom flask. The mixture was stirring at room temperature for 24 hours. The resulting red-pink solid was washed with ethyl acetate, filtered and dried (yield: 57%). As expected for this case, instead of pyridinium monomer quaternary salt, the poly([ViEtPy][Br]) was formed.[56] The poly([ViEtPy][NTf$_2$]) was obtained following the same procedure used for poly([ViEtIm][NTf$_2$]). The obtained orange solid product was washed with water, filtered and dried (yield: 93%).

Poly([Pyr$_{11}$][NTf$_2$]) (Figure 2(c)). This PIL, containing pyrrolidinium cation pendant units, was synthesized solely by carrying out the anion exchange reaction directly into the commercially available poly(diallydimethylammonium) chloride, according to a procedure described elsewhere.[57] The obtained white solid poly([Pyr$_{11}$][NTf$_2$]) was washed with water, filtered and dried (yield: 95%).

Poly([EMTMA][NTf$_2$]) (Figure 2(d)). Initially, 20 g of the commercially available 2-(methacryloyloxy)ethyl trimethylammonium chloride solution (80 wt% in water) was diluted with 200 mL of distilled water and then 0.075 g of the thermal initiator AIBA were added. The free radical polymerization reaction was carried out at 338 K for 3 hours under nitrogen atmosphere. After that, the resulting poly([EMTMA][Cl]) was quantitatively obtained by evaporating the water. Poly([EMTMA][NTf$_2$]) was synthesized using the same anion exchange method described in detail for the preparation of poly([ViEtIm][NTf$_2$]) and a yield of 88% was achieved.

Poly([EMCh][NTf$_2$]) (Figure 2(e)). In this case, the halide forms of both the monomer and the polymer, containing cholinium cation pendant units, were prepared via similar procedures to those previously reported.[58] First, 10 g (63.6 mmol) of 2-(dimethylamino)ethyl methacrylate were mixed with 11.92 g of 2-bromoethanol at 318 K for 24 hours. The resulting product was washed five times with an excess of ethyl acetate and dried under vacuum at room temperature to give the white solid cholinium ethyl methacrylate bromide (yield: 89%). Afterwards, the prepared monomer was polymerized by free radical polymerization in water, which was carried out in sealed round bottom flask under nitrogen atmosphere at 338 K for 3 hours. The resulting aqueous polymer solution was added dropwise to an excess amount of acetone in order to precipitate the poly([EMCh][Br]), which was then filtered and dried in a vacuum oven at 318 K until constant weight was attained (yield: 85%). As it is shown in Figure 2, the same straightforward anion exchange procedure used for the other polycations was also successfully implemented to prepare the poly([EMCh][NTf$_2$]) (yield: 81%).

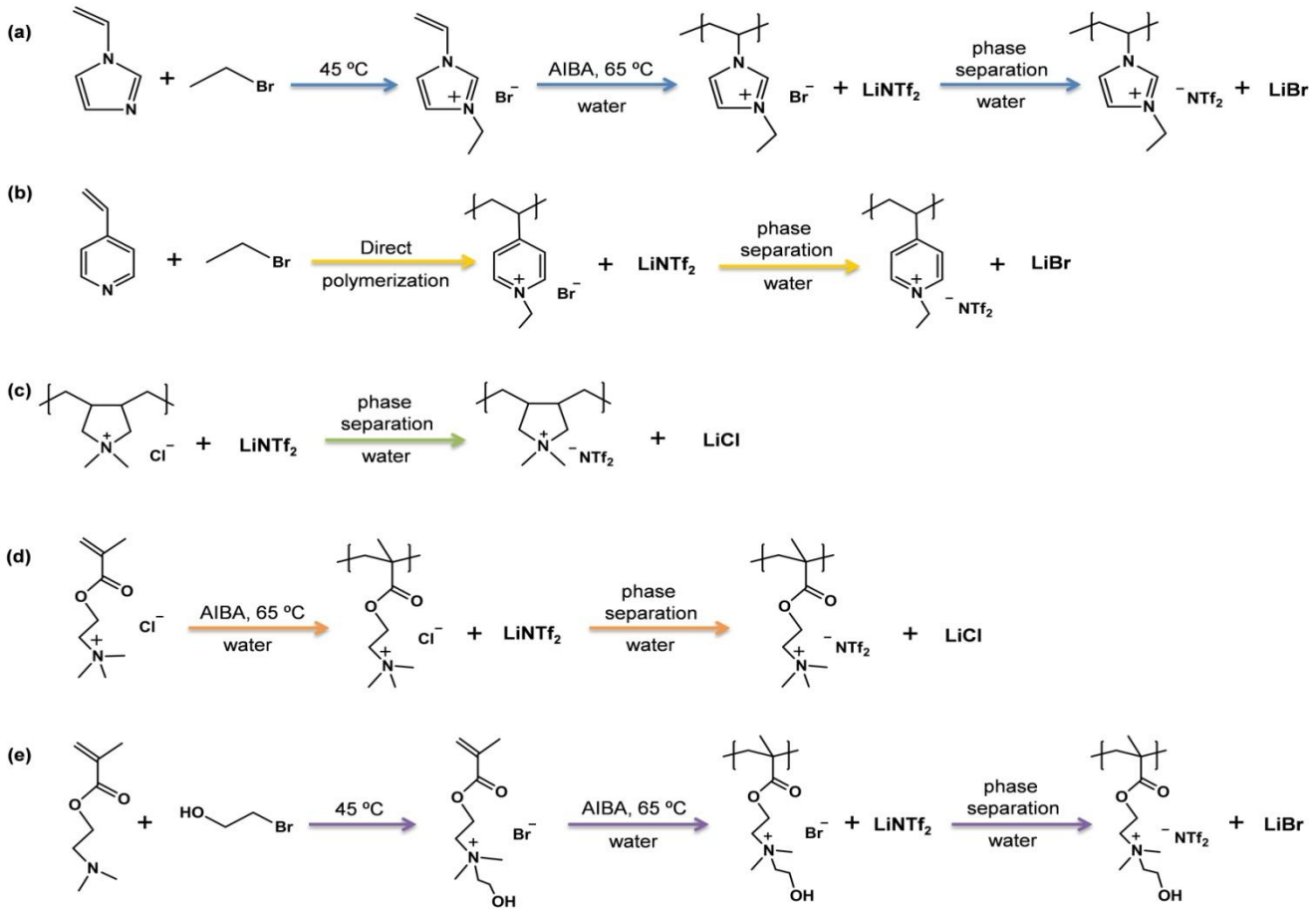

Figure 2| Schemes illustrating the synthesis of the polymeric ionic liquids containing different polycation functionalities (a) imidazolium, (b) pyridinium, (c) pyrrolidinium, (d) ammonium and (e) cholinium, combined with the $[NTf_2]^-$ counter-anion.

3.4. Membranes preparation

Composite membranes based on the synthesized PILs (Figure 1) with free ionic liquids (Figure 3), containing the same anion and structural similar cations to the monomeric of the respective PIL, were prepared by solvent casting method. Initially, 6% (w/v) solutions of each PIL in appropriate solvents were prepared and the corresponding ionic liquids were added in order to obtain solutions with 10 wt% of free IL to the polymer matrix. The solutions were magnetically stirred for 8 hours. Afterwards, transparent and free standing membranes were obtained by casting each solution into poly(tetrafluoroethylene) plates. The experimental conditions of the casting process used to prepare the different composite membranes are presented in Table 1. All solvents were slowly evaporated in a saturated solvent environment in order to obtain dense homogeneous membranes. Finally, all the composites were dried in an oven (338 K) until constant weight was attained. Membrane thicknesses (145–190 μm) were measured using a digital micrometer (Mitutoyo, model MDE-25PJ, Japan). Average thickness was calculated from six measurements taken at different locations of each membrane sample.

Porous hydrophobic poly(vinylidene fluoride) (PVDF) membranes provided by Millipore Corporation (USA), with a pore size of 0.22 μm and average thickness of 125 μm, were used to prepare SILM configurations of the pure ionic liquids according to our previously reported procedure.[22] The thickness of the SILMs was assumed to be equivalent to the membrane filter thickness.

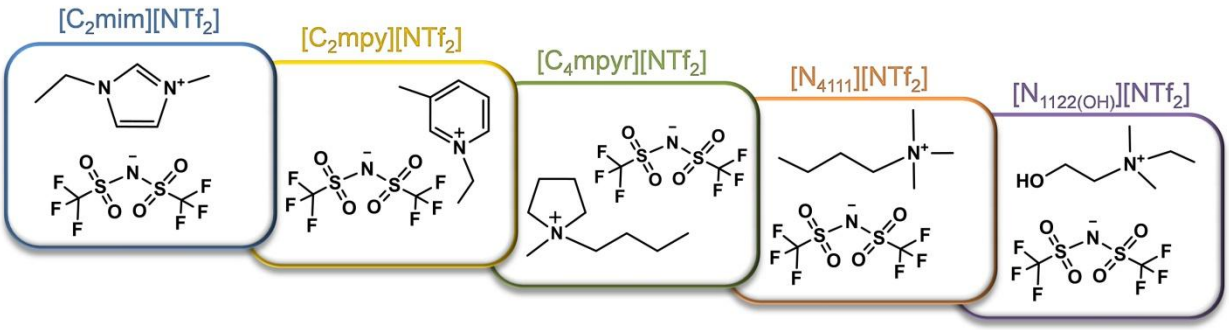

Figure 3| Chemical structures and short names of the ionic liquids used to prepare the composite membranes.

Table 1| Composition and experimental conditions of the procedure used to prepare each composite membrane studied.

Membrane sample	Polymer (PIL)	10 wt % of Ionic Liquid (IL)	Solvent	*T* (K)	Evaporation time (days)
PIL imidazolium–10 IL	Poly([ViEtIm][NTf_2])	[C_2mim][NTf_2]	Acetonitrile	303	3
PIL pyridinium–10 IL	Poly([ViEtPy][NTf_2])	[C_2py][NTf_2]	Acetonitrile	303	3
PIL pyrrolidinium–10 IL	Poly([Pyr_{11}][NTf_2])	[pyr_{14}][NTf_2]	Acetone	298	2
PIL ammonium–10 IL	Poly([EMTMA][NTf_2])	[N_{4111}][NTf_2]	Acetonitrile	303	3
PIL cholinium–10 IL	Poly([EMCh][NTf_2])	[$N_{1122(OH)}$][NTf_2]	Acetonitrile	303	3

3.5. Gas permeation measurements

Single gas permeabilities and diffusivities through the prepared composite membranes were measured using a time-lag apparatus. Details on the construction and operation of this experimental setup are entirely described elsewhere.[41] All the membranes were degassed under vacuum inside the permeation cell during 24 hours before testing. The single gas permeation experiments using CO_2, CH_4, and N_2 were performed at 293 K with a trans-membrane driving force of 100 kPa upstream against initial vacuum downstream (<0.1 kPa). At least three separate experiments of each gas on a membrane sample were performed. Between experiments, the membrane sample was degassed under dynamic vacuum until the downstream pressure was below 0.1 kPa. The membrane thickness was measured before and after testing. Average thickness was calculated from six measurements taken at different locations of each membrane sample. No residual ionic liquid was found inside the permeation cell at the end of the experiments and, similarly, the composite membrane mass remained constant throughout the experiment.

The gas transport through a dense membrane occurs according a solution-diffusion mass transfer mechanism where the permeability (*P*) is related to solubility (*S*) and diffusivity (*D*) as follows:[59]

$$P = S \times D \tag{1}$$

Permeability (*P*) is defined as the steady-state gas flux (*J*) through a membrane under a trans-membrane pressure drop (Δp) and normalized to the unit thickness of the membrane as follows:[60]

$$P = J \frac{\ell}{\Delta p} \tag{2}$$

The flux was determined experimentally using Equation 3, where V^p is the permeate volume, Δp_d is the variation of downstream pressure, *A* is the effective

membrane surface area, *t* is the experimental time, *R* is the Ideal Gas Law constant and *T* is the absolute temperature.

$$J = \frac{V^p \Delta p_d}{AtRT} \tag{3}$$

Diffusivity (*D*) was obtained according to Equation 4. The time-lag parameter (θ), which can be obtained before achieving steady-state flux, was deduced by extrapolating the slope of the linear portion of the p_d vs. *t* curve back to the time axis, where the intercept is equal to θ.[61]

$$D = \frac{\ell^2}{6\theta} \tag{4}$$

After knowing both *P* and *D*, it was also possible to calculate *S* using the relationship shown in Equation (1).

The ideal permeability selectivity (or permselectivity), $\alpha_{i/j}$, was obtained by dividing the permeability of the more permeable specie *i* to the permeability of the less permeable specie *j*. As shown in Equation (5), the permselectivity can also be expressed as the product of the diffusivity selectivity and the solubility selectivity.

$$\alpha_{i/j} = \frac{P_i}{P_j} = \left(\frac{D_i}{D_j}\right) \times \left(\frac{S_i}{S_j}\right) \tag{5}$$

4. Results and Discussion

On the contrary to the pyrrolidinium-PIL with $[NTf_2]^-$ as counter-anion,[41, 62] the other PILs synthesized in the present work, having different polycations and the same counter-anion, cannot be tested as pure PIL gas separation membranes as they are unable to be processed into a mechanically stable flat form membrane using the solvent casting method, due to their brittle nature. In order to measure the CO_2, CH_4, and N_2 permeation properties and evaluate the influence of the polycation functionality on the CO_2 separation performance, composite membranes of the synthesized PILs (Figure 1) with 10 wt% of free ILs (Figure 3) were successfully prepared (Table 1). The ILs were chosen due to their structural similarity to the monomeric unit of the respective PIL. In particular, $[C_4mpyr][NTf_2]$, $[N_{4111}][NTf_2]$ and $[N_{1122(OH)}][NTf_2]$ were used since similar ILs with smaller chains in the cation are solid at room temperature. The exact amount of 10 wt% of free IL was selected because it corresponds to the minimum amount of the plasticizer component (IL) necessary to obtain mechanical stable membranes, which do not break during the gas permeation measurements. Generally, the presence of free IL enables an increase in the CO_2 permeability of PIL-based membranes with little, if no, sacrifice of their CO_2 permselectivities.[42-44] All the prepared composite membranes were homogeneous and exhibited no evidence of phase separation even after several months of storage under ambient conditions.

4.1. Gas permeability, diffusivity and solubility

The measured gas permeability and diffusivity values in the composite membranes containing the PILs with different polycations and 10 wt% of free IL are presented in Figure 4 and Figure 5, respectively, while the gas solubility values calculated using Equation (1) are shown in Figure 6. It should be pointed out that

even though imidazolium-PILs have been extensively used as polymer matrices to prepare CO_2 separation membranes,[35-40, 42-48] the gas permeation properties of PIL-based membranes containing pyridinium, ammonium and cholinium cations in the polymer backbone are reported here for the first time. Concerning the pyrrolidinium-PIL, a comparison of CO_2, CH_4, and N_2 permeabilities measured in this work with values previously determined by us for similar membranes is shown in Table 2. The permeability values of the three gases obtained in the PIL pyrrolidinium–10 IL are between those reported for the pure PIL and the composite membrane with 20 wt% of the same free IL ($[C_4mpyr][NTf_2]$). Although an exact comparison of the results cannot be made due to the different IL contents used, this behavior when scaling the gas permeability with the amount of free IL incorporated into the PIL membranes is in agreement to what has been recognized by different authors.[30, 38, 41, 62, 63]

Table 2| Comparison of CO_2, CH_4, and N_2 permeabilities (P)[a] measured in this work with the values previously determined using the same experimental conditions (293 K with a trans-membrane pressure differential of 100 kPa) for pyrrolidinium-based PILs.[b]

Membrane	P CO_2	P CH_4	P N_2
Pure PIL pyrrolidinium [c]	5.09 ± 0.03	0.18 ± 0.01	0.23 ± 0.01
PIL pyrrolidinium–10 IL	11.5 ± 0.09	0.41 ± 0.01	0.40 ± 0.01
PIL pyrrolidinium–20 IL[c]	25 ± 0.16	0.98 ± 0.03	0.78 ± 0.01

[a] Barrer (1 Barrer = 10^{-10} cm^3(STP)cm cm^{-2} s^{-1} $cmHg^{-1}$)

[b] The listed uncertainties represent the standard deviations, based on three experiments.

[c] Values taken from Tomé *et al*.[41]

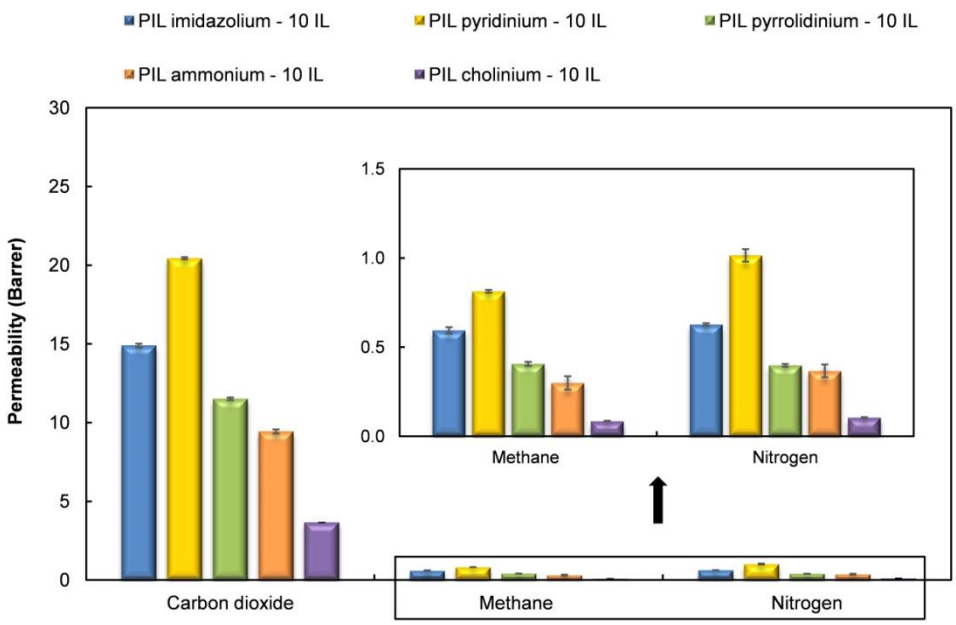

Figure 4| Gas permeabilities (1 Barrer = 10^{-10} cm^3(STP)cm cm^{-2} s^{-1} $cmHg^{-1}$) through the prepared composite membranes. Error bars represent standard deviations based on three experimental replicas.

The results presented in Figure 4 show that the composite membranes containing distinct PILs and 10 wt% of free IL possess gas permeabilities that are substantially different than those of PIL imidazolium–10 IL. The highest gas permeabilities were obtained for PIL pyridinium-based membrane, whilst the PIL cholinium exhibited the lowest gas permeabilities. In fact, the relative gas permeability enhancement or reduction is clearly dependent on the polycation backbone (Figure 4). For example, the obtained CO_2, CH_4, and N_2 permeabilities of PIL pyridinium–10 IL were 20.4, 0.81 and 1.01 Barrer, respectively, which are about 1.3 times higher than those achieved with PIL imidazolium-based membrane. In contrast, the PIL pyrrolidinium–10 IL presented a CO_2 permeability of 11.5 Barrer, which is roughly 1.3 times smaller than that of PIL imidazolium (14.9 Barrer). Moreover, the gas permeability reductions between PIL imidazolium–10 IL and PIL cholinium–10IL, in which the CO_2, CH_4, and N_2

permeabilities decreased by 303%, 556% and 473%, are larger than those between PIL imidazolium–10 IL and PIL ammonium–10 IL, where permeability reductions of only 59%, 97% and 70% occurred, respectively. Although PIL cholinium has a bulkier tetra-alkyl ammonium pendant unit, connected to the poly(methyl methacrylate), backbone than that of analogous PIL ammonium, the presence of the hydroxyl group seems to increase linear chain packing, certainly through hydrogen bond interactions, contributing to a more polymer packed membrane with higher resistance to gas diffusion.

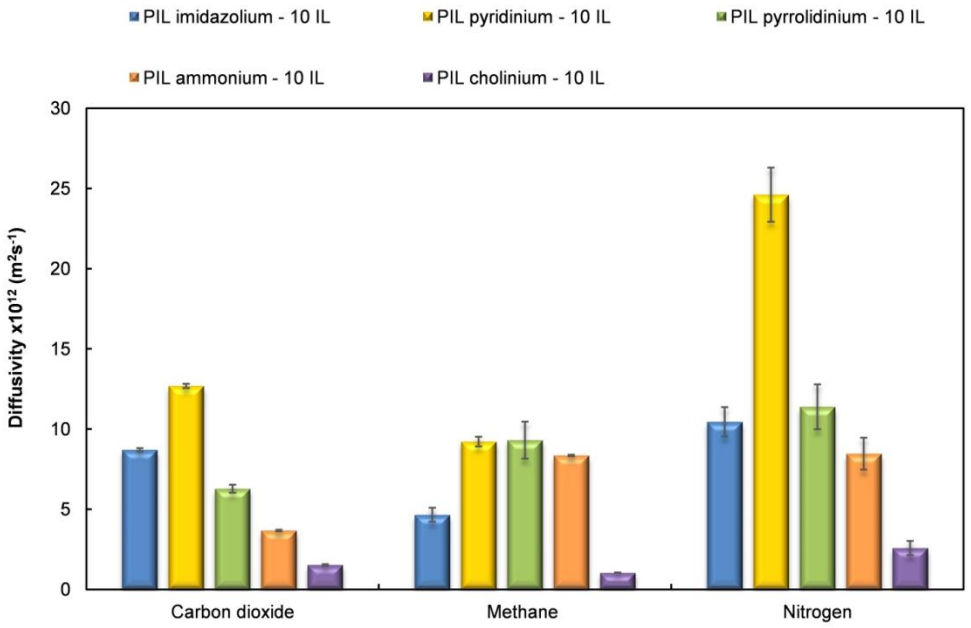

Figure 5| Gas diffusivities through the prepared composite membranes. Error bars represent standard deviations based on three experimental replicas.

We also noticed that diffusivity is the primary factor differentiating the gas permeabilities among the composite membranes comprising the PILs with different polycations. For instance, the CO_2 and N_2 permeabilities (Figure 4) are related with their respective gas diffusivities (Figure 5), both following the order of the polycation backbone variation as: PIL pyridinium > PIL imidazolium ≥ PIL

pyrrolidinium > PIL ammonium > PIL cholinium. The obtained results clearly show that PILs with pyridinium or imidazolium polycations exhibited higher CO_2 permeabilities and diffusivities compared to those having tetra-alkyl ammonium pendant units. Conversely, the opposite behavior occurs in CO_2 solubility. As it can be seen from Figure 6, tetra-alkyl ammonium-based PIL, namely pyrrolidinium, ammonium and cholinium, possess higher CO_2 solubility than imidazolium- and pyridinium-based PILs, which can be caused by their localized charge density that results in stronger interactions with CO_2, and consequently contributes for lower CO_2 permeabilities. These findings also suggest that the CO_2 solubility in the prepared composite membranes can be improved by increasing the polycation polarity.

Overall, our results demonstrate that the type of polycation influences the gas transport properties. Depending on the chemical structure of the polycation, the PIL chains interact and pack differently and thus PIL–IL composite membranes with different gas permeabilities, diffusivities and solubilities can be obtained.

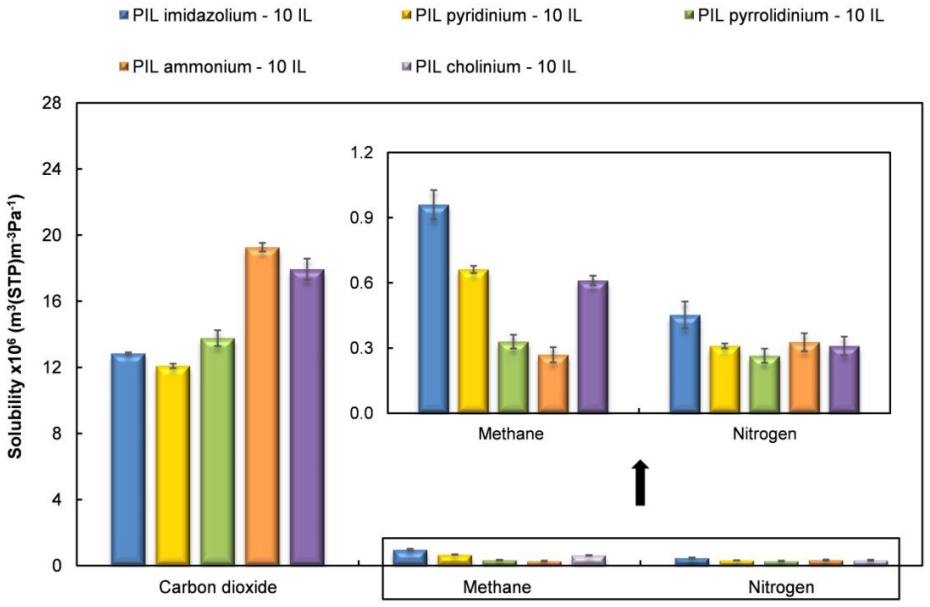

Figure 6| Gas solubilities in the prepared composite membranes, calculated using Equation (1).

4.2. CO_2 separation performance

The measured CO_2 permeabilities and both the CO_2/CH_4 and CO_2/N_2 permselectivities of all the studied composite membrane are summarized in Table 3. These results are also plotted on the so-called Robeson plots,[64] where the permselectivity between CO_2 and CH_4 (or N_2) is plotted against the CO_2 permeability. The upper bound was empirically defined using a wide range of experimental data for each separation,[64] and represents the current limit of gas permeability *vs*. permselectivity for known polymeric gas separation membranes. Therefore, the comparison of CO_2/CH_4 and CO_2/N_2 separation performances between the results obtained in this work and the previously published data for other PIL-based membranes can be evaluated, respectively, in Figure 7(a) and Figure 7(b).

Table 3 Single CO_2 permeability (P)[a] and ideal permselectivities (α) of the membranes studied.[b]

Membrane sample	P CO_2	α CO_2/CH_4	α CO_2/N_2
PIL imidazolium–10 IL	14.9 ± 0.12	25.1 ± 1.0	23.7 ± 0.5
PIL pyridinium–10 IL	20.4 ± 0.07	25.1 ± 0.3	20.1 ± 0.8
PIL pyrrolidinium–10 IL	11.5 ± 0.09	28.3 ± 1.0	28.9 ± 0.8
PIL ammonium–10 IL	9.44 ± 0.13	31.5 ± 4.4	25.8 ± 2.9
PIL cholinium–10 IL	3.66 ± 0.01	43.0 ± 1.1	34.7 ± 0.9
SILM $[C_2mim][NTf_2]$[c]	589 ± 1.0	18.1 ± 0.3	35.5 ± 0.3
SILM $[C_2mpy][NTf_2]$	536 ± 3.3	17.6 ± 0.2	31.9 ± 0.6
SILM $[C_4mpyr][NTf_2]$[d]	340 ± 0.7	14.0 ± 0.1	28.4 ± 0.3
SILM $[N_{4111}][NTf_2]$	333 ± 0.4	15.4 ± 0.1	27.2 ± 0.3
SILM $[N_{1122OH}][NTf_2]$	84 ± 0.2	21.8 ± 0.1	37.4 ± 0.3

[a] Barrer (1 Barrer = 10^{-10} cm^3(STP)cm cm^{-2} s^{-1} $cmHg^{-1}$)

[b] The listed uncertainties represent the standard deviations, based on three experiments.

[c] Values taken from Tomé *et al.*[22]

[d] Values taken from Tomé *et al.*[41]

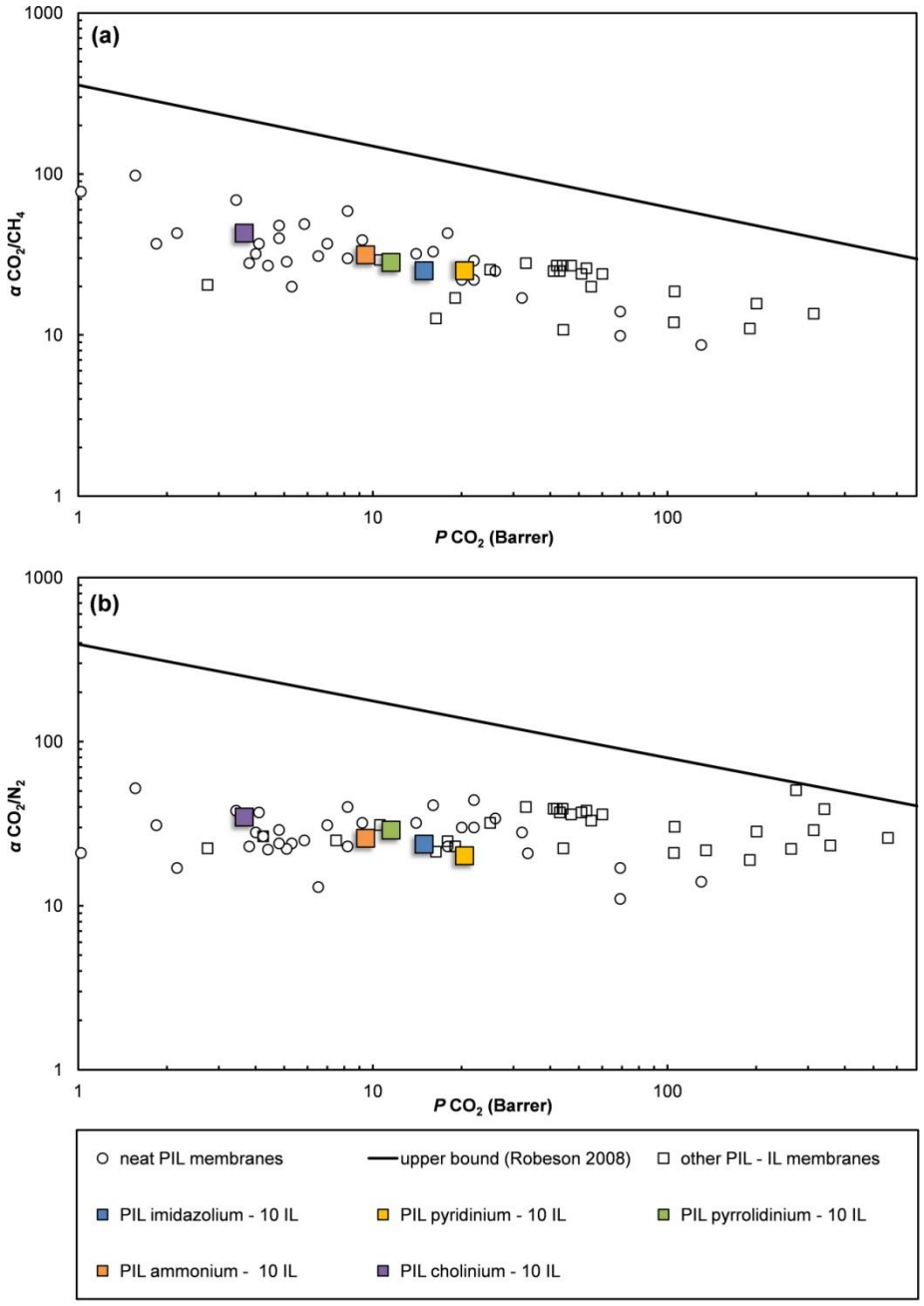

Figure 7| CO_2 separation performance of the studied composite membranes plotted on (a) CO_2/CH_4 and (b) CO_2/N_2 Robeson plots. The experimental error is within the data points. Data are plotted on a log-log scale and the upper bound for each gas pair is adapted from Robeson.[64] For comparison, also plotted in (a) and (b) are literature data previously reported for (□) other PIL–IL membranes,[37, 39-45, 47, 49] and (○) neat PIL membranes.[36, 37, 39-41, 53, 65, 66]

In contrast to what has been observed for PIL–IL membranes with IL contents higher than 20 wt%,[36-38, 41, 43, 44, 49] and also for SILMs,[22, 25, 27, 28] the Robeson plots indicate that CO_2/CH_4 (Figure 7(a)) is a more favorable separation than CO_2/N_2 (Figure 7(b)) for the composite membranes herein prepared. With the exception of PIL pyrrolidinium–10 IL, that presents similar permselectivities values for both separations, the CO_2/CH_4 permselectivity is always higher than the CO_2/N_2 permselectivity (Table 3) since the N_2 permeability is greater than that of CH_4 in the prepared composite membranes. Nevertheless, these results are in agreement with previous studies on pure PIL membranes.[41, 66] It means that, in the case of PIL–IL membranes blended with only 10 wt% of free IL, the polymer matrix has great influence on their permselectivity properties. Looking at the results presented in Table 3, the composite membranes comprising the different PILs have indeed intrinsically superior CO_2/CH_4 permselectivities, whereas the CO_2/N_2 values are smaller than those of their ionic liquid analogues in SILM configurations.

Figure 7 shows that the CO_2 separation performances of the prepared composite membranes with 10 wt% of free IL are bellow the CO_2/CH_4 and CO_2/N_2 upper bounds, close to available literature data for the neat PIL membranes. However, it can be also observed that the use of PILs possessing different polycation backbones impacts the CO_2/CH_4 and CO_2/N_2 separation performance of the composite membranes. For example, the use of PIL pyridinium increases the CO_2 permeability without affecting CO_2/CH_4 permselectivity, but it also decreases the CO_2/N_2 permselectivity of the PIL pyridinium–10 IL compared to PIL imidazolium–10 IL. On the other hand, the presence of tetra-alkyl ammonium-based PILs (pyrrolidinium, ammonium and cholinium) decreases the CO_2 permeability of the composite, whereas they promote improved CO_2/CH_4 and CO_2/N_2 permselectivities (Table 3) compared to those of the composite membrane comprising the PIL imidazolium. Even though PIL cholinium promotes

the lowest gas permeabilities (Figure 4) and diffusivities (Figure 5), remarkable CO_2/CH_4 and CO_2/N_2 permselectivities of 43.0 and 34.7, respectively, can be achieved using this PIL as polymer matrix. This behavior is in accordance with the well know tradeoff between flux and selectivity, which means that improvements in polymeric membrane permselectivities are generally associated to a reduction of their gas permeabilities. Taking into account that the diffusivity selectivities of all the studied membranes are between 0.4 and 1.9, the membranes of tetra-alkyl ammonium-based PILs are intrinsically more CO_2 permselective, probably due to their high CO_2/CH_4 (29.4 – 71.6) and CO_2/N_2 (52 – 59) solubility selectivities compared to those (CO_2/CH_4 13.4 – 18.3, CO_2/N_2 28.4 – 39.0) obtained when PIL imidazolium or PIL pyridinium are used.

All the above mentioned evidences contribute to understand the behavior and show the influence of polycation variation on the CO_2 separation performance of these materials. It is clear that the structure of the polycation functionality can play an important role in the gas transport properties through PIL–IL membranes.

5. Conclusions

Five polymeric ionic liquids containing different polycations and $[NTf_2]^-$ as counter-anion were synthesized by suitable reaction schemes. Since the nature of the pure PILs was very brittle and their films easily broke, composite membranes with 10 wt% of free ILs having similar chemical structures to each PIL monomeric unit were prepared and their single CO_2, CH_4, and N_2 permeation properties were measured.

The results showed that the membranes based on the tetra-alkyl ammonium-based PILs (pyrrolidinium, ammonium and cholinium) generally have lower gas permeabilities and diffusivities, whereas they present higher CO_2/CH_4 and CO_2/N_2 permselectivities than those of membranes containing PIL imidazolium and

pyridinium. The gas permeabilities, diffusivities and solubilities in the composite membranes were found to be dependent on the PIL polycation backbone. Moreover, the Robeson plots showed that CO_2/CH_4 is a more favorable separation for the prepared composite membranes, but their performance is still bellow the upper bounds (from 2008) for both separations CO_2/CH_4 and CO_2/N_2. Overall, the results of this work not only point out that the PIL polycation nature can influence the CO_2 separation in PIL–IL composite membranes, but also reaffirm that to better understand and thus improve the gas transport through these type of membranes it is necessary to further explore the available high diversity of chemical structures that are inherent to PILs.

Even though it is evident that the PIL polycation variation alone cannot promote the large improvement in gas permeability required for these membranes to be technologically competitive, the knowledge gained from this work, particularly regarding the relationships between PIL structure and gas transport properties, is undoubtedly important for the development of PIL-based membranes with superior CO_2 separation performances.

6. Acknowledgements

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Chapter 5

Pyrrolidinium-based polymeric ionic liquid materials for CO_2 separation

Adapted from: **L.C. Tomé,** D. Mecerreyes, C.S.R. Freire, L.P.N. Rebelo, I.M. Marrucho, Pyrrolidinium-based polymeric ionic liquid materials: New perspectives for CO_2 separation membranes, *J. Membr. Sci.*, 2013, **428**, 260-266. (highly cited paper 2013, top 1%).

The author was involved in all the experimental work, as well as on the discussion and preparation of the manuscript.

1. Abstract

The CO_2 separation performance of a new series of polymeric ionic liquid (PIL) composite membranes based on poly([pyr_{11}][NTf_2]) by the addition of 0, 20, 40, 60, 80 and 100 wt% of [C_4mpyr][NTf_2] were measured in order to establish the feasibility of using these composites as membranes for flue gas separation and natural gas purification. This study evaluates membranes within the whole range of compositions, from pure ionic liquid (IL) to pure polymer (PIL). The results show that the permeability of the three gases (CO_2, CH_4, and N_2), in the IL is two orders of magnitude higher than that of the PIL. The preparation of composite membranes increases the permeability of all three gases, overcoming the hindered diffusion of gas in the polymer. The composites also promote increased permselectivity for CO_2/N_2, while the opposite behavior was found for CO_2/CH_4. Robeson plots were used to evaluate and understand the performance of the prepared membranes for the two selected gas separations. The addition of free IL to the polymer system has the main role in the permselectivity of the prepared composites.

2. Introduction

In the field of energy, natural gas is an essential bridge to a clean, low carbon, renewable energy era. Regulations regarding the processing and transportation of natural gas require the removal of contaminant compounds such as H_2S, CO_2, and heavier hydrocarbons.[1] In addition, the increasing atmospheric concentrations of greenhouse gases, specifically CO_2, is of particular concern and new cost-effective, high performance technologies for carbon capture and storage are being researched.[2] In fact, the main strategies for natural gas processing are identical to those used for CO_2 capture, since both make use of solvent absorption with amines, adsorption with porous solids and cryogenic separation.[1, 3] Although

amine-based processes are highly efficient, they are not a long-term environmental and economical solution because of the high energy costs associated with the regeneration of amines.[4] Thus, research targeted at developing new approaches for CO_2 separation has been undertaken.

Membranes offer fundamental engineering and economic advantages over other separation technologies in CO_2 capture from fossil fuels flue gas streams and also in natural gas separation and purification. The major drawback in membrane operation, other than deterioration, concerns the low selectivity of the material. It is well known that for most membranes there is a tradeoff between selectivity and permeability, meaning that a highly permeable membrane is obtained at the cost of poor selectivity and vice-versa.[5] Overcoming this tradeoff is the focus of much research on polymeric membranes for gas separations.

In the past few years, the field of ionic liquids has blossomed at the interface of many disciplines. ILs are low-melting-point salts and, apart from their broad definition as compounds with a combination of attractive properties such as negligible volatility,[6] thermal stability,[7] and low flammability,[8] their most attractive feature is their tunability which allows for the design of ILs for each specific purpose.[9] The use of ILs for gas separation processes has received growing attention in recent years, particularly in applications involving CO_2 separations, due to the high levels of solubility and selectivity of CO_2 relative to CH_4 and N_2.[10-16] A large amount of work has been published on the permeation properties of gases such as CO_2, N_2, and CH_4 in imidazolium-based ILs,[17-28] and various other families of ILs (pyridinium,[29, 30] phosphonium and ammonium[31]). Different approaches have been taken, the most important being the use of supported ionic liquid membranes (SILMs) by impregnating the IL into a porous polymer support. SILMs are considered a very attractive methodology because small amounts of IL are required. SILMs have shown good performance with permeabilities/selectivities that are consistently close to the Robeson plot upper bound.[17, 25, 32] Nevertheless,

their application in industry is limited to low transmembrane pressure differentials, due to the risk of expelling the IL from the support pores and destroying the SILM.[14]

A way to take advantage of ILs for CO_2 separation and simultaneously overcome the SILM drawback is to polymerize IL monomers and prepare solid thin membranes.[33] There has been growing interest in the polymeric form of ILs since this new class of functional polymers combines some of the unique properties of ILs with the improved mechanical and physical-chemical properties of polymers.[34] Tang *et al.* showed that PILs exhibit even higher CO_2 absorption capacity and faster absorption/desorption rates than ILs.[35] Noble *et al.* studied several structurally different imidazolium-based PILs for CO_2 separation and showed that these membranes are more stable than conventional ones and possess CO_2/N_2 and CO_2/CH_4 separation selectivities on par or greater than those observed for SILMs.[17, 36-38] The same authors also found that appropriate structural variations of the imidazolium cation, cross-linking of PILs and PIL composite membranes with free IL, resulted in high performance gas separation membranes.[37-44] Although patterns are emerging as to which PILs enhance CO_2 separation, considerable research is still required for a complete understanding of the relationship between molecular composition, macromolecular structure and gas permeation properties. All the studies published to date involving PIL composite membranes for gas separation are limited to the imidazolium cation,[37-45] and fail to provide a comprehensive view of the whole material range, from PILs to ILs, encompassing PIL–IL composites of other different cations.

In this work, we evaluate the CO_2 separation performance of a new series of PIL–IL composite membranes based on poly([pyr_{11}][NTf_2]). This pyrrolidinium-based PILs is particularly simple to prepare, since a commercially available polymer is used as a starting material and the PIL is prepared by way of metathesis. Moreover, the monomeric unit which contains the pyrrolidinium

functionality is less toxic than the imidazolium counterparts [46], usually used in PILs. The $[NTf_2]^-$ anion was chosen due its CO_2-phylic behavior and high thermal stability. The $[C_4mpyr][NTf_2]$ was chosen as the free IL due to its structural similarity to the monomeric unit of the PIL and also because similar ionic liquids with smaller chains in the cation are solid at room temperature. The chemical structures of the materials used are shown in Figure 1.

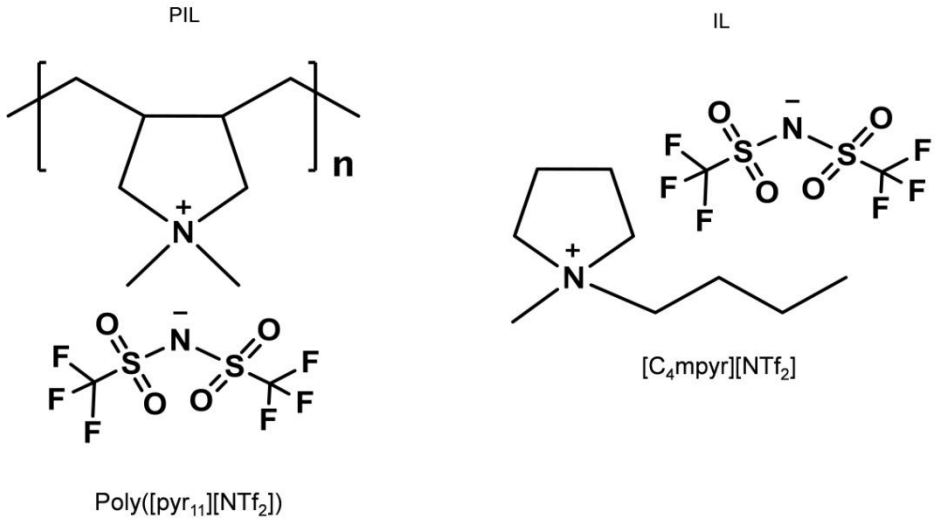

Figure 1| Chemical structures of the pyrrolidinium-based polymer and ionic liquid.

3. Experimental Section

3.1. Materials

1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ($[C_4mpyr][NTf_2]$) (99 wt% pure) was supplied by IoLiTec GmbH. Poly(diallyldimethylammonium) chloride solution (average Mw 400 000–500 000, 20 wt% in H_2O) and lithium bis(trifluoromethylsulfonyl)imide ($LiNTf_2$, 99%) were purchased from Sigma-Aldrich and IoLiTec GmbH, respectively, and used as received. Durapore porous hydrophobic polyvinylidene fluoride (PVDF) membranes, with a pore size of 0.22

μm, average thickness of 125 μm, from Millipore Corporation (USA) were used to support the ionic liquids. To calibrate the time-lag apparatus, LDPE with density of 0.920 g cm^{-3} was purchased from Silvex (Portugal). All gases were supplied by Air Liquid and were of at least 99.99% purity. Gases were used with no further purification.

3.2. Synthesis of the pyrrolidinium-based polymeric ionic liquid

Polymeric ionic liquid containing pyrrolidinium pendants units and NTf_2 as counter-anion (Figure 1) was synthesized by an anion exchange reaction from the commercially available polymer poly(diallyldimethylammonium) chloride following an established procedure.[47] The obtained white solid, poly([pyr_{11}][NTf_2]), was then washed with water, filtered and dried until constant weight was attained.

3.3. Preparation of poly([pyr_{11}][NTf_2])-[C_4mpyr][NTf_2] membranes

Poly([pyr_{11}][NTf_2]) membranes, with and without free IL, were prepared by the solvent casting method. Initially, poly([pyr_{11}][NTf_2]) was dissolved in acetone (12% (w/v)). Subsequently, different amounts of IL were added in order to obtain solutions with different wt% of IL to the polymer matrix (Table 1). The solutions were magnetically stirred for 8 hours. Transparent and free standing membranes (Figure 2) were obtained by casting each solution into Petri dishes and the acetone was left to evaporate at room temperature for 48 hours, with the exception of IL compositions higher than 60 wt%, where liquid mixtures were obtained. Solvent evaporation took place slowly and in a saturated acetone environment in order to obtain homogeneous membranes. Membrane thicknesses (90 – 120 μm) were measured using a digital micrometer (Mitutoyo, model MDE-25PJ, Japan). The prepared solid composite membranes exhibited no

evidence of phase separation between the PIL and IL components, even after storing at ambient conditions for several months.

Table 1| Identification of the pyrrolidinium-based membranes prepared.

Membrane	wt% poly([pyr_{11}][NTf_2])	wt% [C_4mpyr][NTf_2]	PVDF as supporting material
Pure PIL	100	-	-
PIL–20 IL	80	20	-
PIL–40 IL	60	40	-
PIL–60 IL	40	60	-
PIL–80 IL	20	80	✓
Pure IL	-	100	✓

3.4. Preparation of supported ionic liquid membranes

The supported liquid membranes of the pure IL ([C_4mpyr][NTf_2]) and the liquid mixture of poly([pyr_{11}][NTf_2]) with 80 wt% of IL were prepared using a polymeric porous membrane (PVDF) as the supporting material (Table 1). These membranes are characterized by their high chemical resistance and have been used in other works for the same purpose.[15, 27] To prepare SILMs, a PVDF membrane was placed inside a desiccator and vacuum was applied for 1 hour, in order to remove air from the membrane pores. Then, 1 mL of the IL (previously dried) was spread under vacuum on the membrane surface, using a syringe that has been previously introduced in the dessicator for this purpose, and vacuum was applied for another 1 hour. As the IL penetrated into the membrane pores, the membrane became transparent. After this immobilization procedure, the membrane was taken out of the desiccator and its surface was cleaned with a soft tissue paper to remove the excess of IL. The amount of IL immobilized was determined gravimetrically by weighing the membrane before and after immobilization.

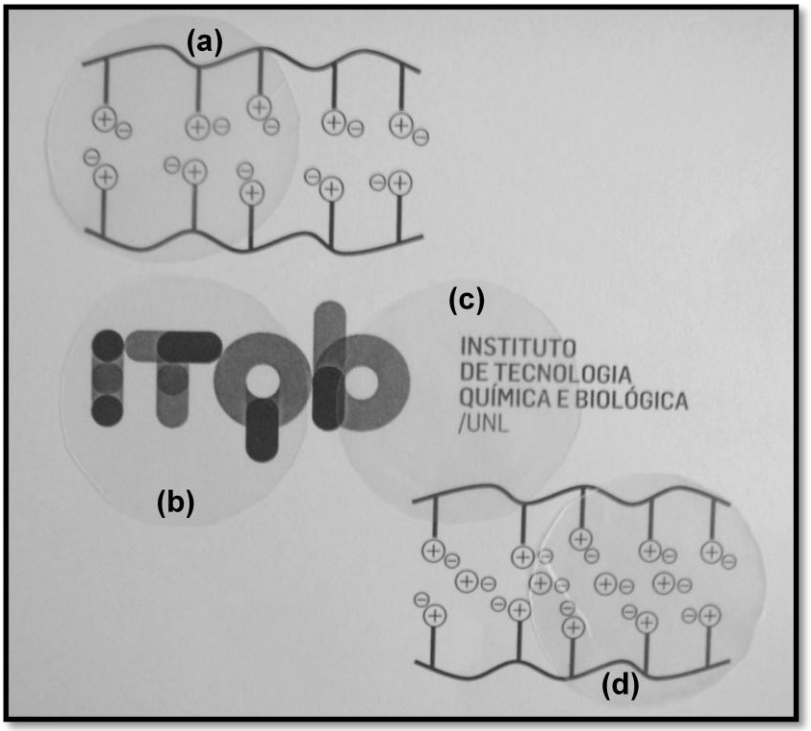

Figure 2| Examples of prepared membranes: (a) pure PIL, (b) PIL–20 IL (c) PIL–40 IL and (d) PIL–60 IL.

3.5. Gas permeation measurements

Two methods have commonly been used to measure the permeation of pure gases through dense polymer membranes, one differential and one integral [48]. Despite the advantages and disadvantages, the integral method, or the so-called time-lag method, is undoubtedly more frequently used which allows for the simultaneous determination of permeability and diffusivity.[49]

A diagram of the time-lag apparatus is shown in Figure 3. It is composed of two stainless steel tanks, one of them with 5 dm^3 (feed) and the other with (34.2 ± 0.2) cm^3 (permeate). Both reservoirs are connected to the permeation cell, which has 13.9 cm^2 of effective area. This cell is composed of a sintered disk to support the membrane and a viton O-ring to seal the cell. Two sensors controlled pressure, one at the feed tank (S-10 WIKA, 6 bar, ± 0.05% FS, P1) and in the

permeate tank there was a high precision absolute pressure sensor (MKS e-Baratron, ref. 628 C, 13.33 kPa, 0.001% FS, P2) for measuring pressure variations. The time-lag unit was placed inside a thermostatic cabinet with a precision of ± 0.05 K. A rotatory high vacuum pump (BOC Edwards, RV3) guaranteed vacuum conditions.

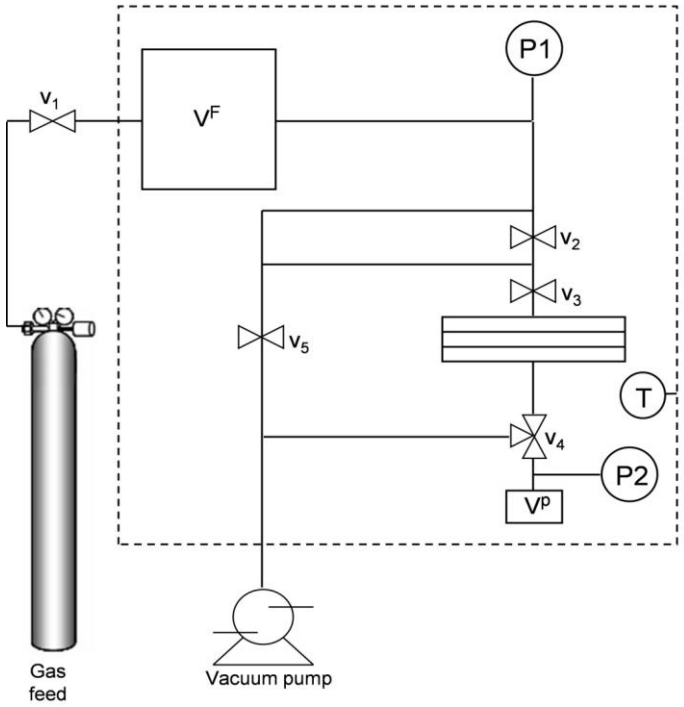

Figure 3| The time-lag apparatus. P represents the pressure sensors, V the manual valves, V^F the feed tank, V^p the permeate tank and T a thermostatic air bath.

The permeability of dense membranes to permanent gases is normally described by the solution-diffusion model.[50] The determination of the mass transport parameters by the time-lag method is based on the downstream pressure history, monitored herein by a pressure sensor P2. At quasi steady-state conditions, the pressure history derivative indicates the permeate flux. This method assumes that the pressure increment is negligible or can account for gas

permeation. Assuming a homogeneous membrane and ideal gas behavior, permeate flux (*J*) can be obtained:[51, 52]

$$J = \frac{n}{At} = \frac{V^p \Delta p_d}{AtRT} \quad (1)$$

where *A* is the effective area of membrane, ΔP_d is the variation of downstream pressure, V^p is the permeate volume, *t* is time, *n* is the quantity of mater, *R* is the gas constant and *T* is absolute temperature. Thus, the permeability (*P*) can be calculated using the following equation:

$$P = J \frac{\ell}{\Delta p} \quad (2)$$

where ℓ is the membrane thickness and Δ*p* is the difference in pressure (driving force). The time-lag parameter (θ), which can be obtained before achieving steady state flux, relates to the diffusivity (*D*) as follows:[53]

$$D = \frac{\ell^2}{6\theta} \quad (3)$$

Since permeability is the product of solubility and diffusivity, it is possible to calculate the solubility coefficient (*S*):[50]

$$P = S \times D \quad (4)$$

The permselectivity (or ideal separation factor), *α*, is the ratio of the permeabilities of the two individual permeating species (*i* and *j*) and is a measure of how well a membrane discerns one gas from another. Permselectivity can also be expressed as the product of the diffusivity selectivity and the solubility selectivity as follows:

$$\alpha_{i/j} = \frac{P_i}{P_j} = \left(\frac{D_i}{D_j}\right) \times \left(\frac{S_i}{S_j}\right) \quad (5)$$

Gas permeation experiments using CO_2, CH_4 and N_2 were performed at 294 K with an upstream pressure of 100 kPa and vacuum (< 0.1 kPa) as the initial downstream pressure. Each membrane was degassed under vacuum during 24 hours inside the permeation apparatus. The thickness of the membranes was measured before and after testing. Average thickness was calculated from six measurements taken at different locations in each membrane sample. All permeation data were performed in triplicate (e.g. three separate experiments of each gas) on a single membrane. The membrane was degassed under vacuum between each run until the downstream pressure was below 0.1 kPa.

No residual ionic liquid was found inside the permeation cell at the end of the experiments and, similarly, the membrane mass remained constant throughout the experiment.

4. Results and Discussion

The PIL used was obtained by way of a metathesis reaction of the halide anion of a commercially available polymer for a more hydrophobic counter-anion, followed by polymer precipitation in water. Thus, only a simple purification step by filtration was required to obtain a very pure polymer.[47] This synthetic route is straightforward and less complicated than that used to prepare the imidazolium-based PILs which have been tested as CO_2 separation membranes, since this strategy involves a number of organic syntheses and purification steps at the monomer level, as well as the need to control polymerization conditions.[37, 38, 42, 43, 45, 54] Consequently, pyrrolidinium-based polymeric ionic liquids were selected to conduct our studies. Composites of poly([pyr_{11}][NTf_2]) with free IL were prepared. It should be pointed out that ILs within PILs are different from traditional plasticizers in conventional polymers due, not only to their negligible volatility,[6] but also to their ability to strongly interact with the charged backbone of PIL through electrostatic interactions.

4.1. Gas permeation properties and permselectivity

To ensure the proper operation of the time-lag apparatus, the permeation of CO_2 in blown LDPE films was measured. Using a 54 μm thick membrane, the measured permeability and diffusivity towards CO_2 at 298 K were 12.6 Barrer and 3.95×10^{-11} $m^2 s^{-1}$, respectively. These values are in good agreement with those measured by Michaels and Bixler [55] for the same system, with a permeability of 12.7 Barrer and a diffusivity of 3.72×10^{-11} $m^2 s^{-1}$.

To the best of our knowledge, this is the first published report of gas permeation properties of both polymeric ionic liquid membranes using a pyrrolidinium cation in the polymer backbone and pyrrolidinium-based IL supported membranes. Permeability and permselectivity values of the measured gases in the pyrrolidinium-based membranes are summarized in Table 2, while diffusivity and solubility values are shown in Figure 4 and Figure 5, respectively.

Table 2| Gas permeability (P)[a] and ideal permselectivity (α) of the pyrrolidinium-based membranes.[b]

Membrane	P CO_2	P CH_4	P N_2	α CO_2/CH_4	α CO_2/N_2
Pure PIL	5.09 ± 0.03	0.18 ± 0.01	0.23 ± 0.01	28.6 ± 1.8	22.2 ± 1.1
PIL-20 IL	25.0 ± 0.2	0.98 ± 0.03	0.78 ± 0.01	25.5 ± 1.0	32.0 ± 0.7
PIL-40 IL	105.5 ± 0.2	5.65 ± 0.01	3.49 ± 0.18	18.7 ± 0.1	30.3 ± 1.6
PIL-60 IL	200 ± 1	12.8 ± 0.1	7.06 ± 0.03	15.7 ± 0.2	28.3 ± 0.3
PIL-80 IL	313 ± 1	23.0 ± 0.1	10.8 ± 0.1	13.6 ± 0.1	28.9 ± 0.4
Pure IL	340 ± 1	24.2 ± 0.1	12.0 ± 0.1	14.0 ± 0.1	28.4 ± 0.3

[a] Barrer (1 Barrer = 10^{-10} cm^3(STP)cm cm^{-2} s^{-1} $cmHg^{-1}$)

[b] The listed uncertainties represent the standard deviations, based on three experiments.

The measured permeability values of pure PIL towards CO_2, CH_4 and N_2 (Table 2) are of the same order of magnitude of those reported in the literature for other

PILs also determined by the time-lag method.[37, 38, 42] This method as used herein minimized water content since vacuum was applied to the membrane until a constant pressure was obtained before starting the experiment.

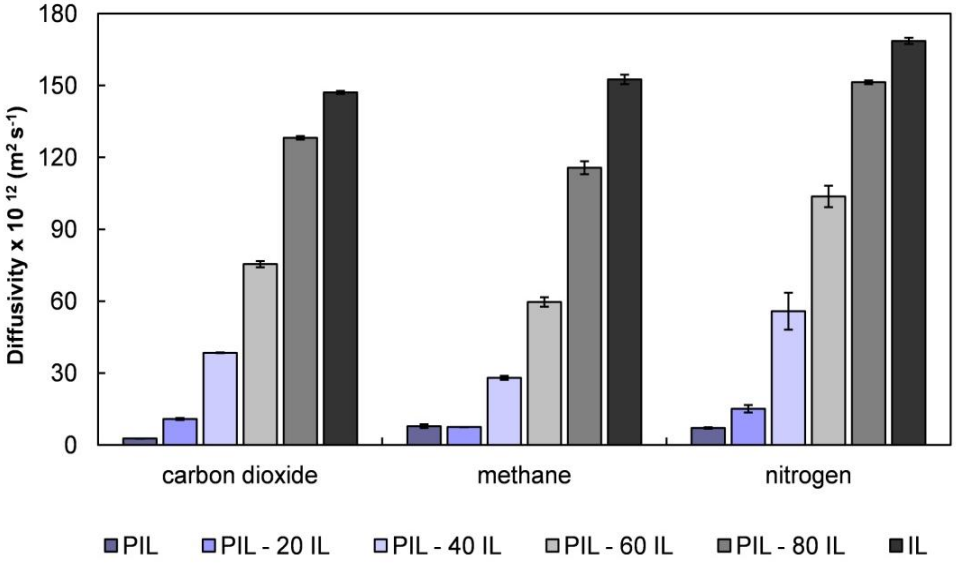

Figure 4| Gas diffusivity through the pyrrolidinium-based membranes. Error bars represent standard deviations based on three experimental replicas.

Table 2 shows that opposite trends in the permselectivities for the separation of CO_2/CH_4 and CO_2/N_2 were obtained. While α CO_2/CH_4 is larger in the PIL than in the IL, the opposite behavior is found for α CO_2/N_2. This difference in performance can be attributed to the different properties of each material. Thus, the IL permselectivity values can be attributed to the quicker gas diffusion of N_2 than CH_4, while roughly the same diffusivity is obtained for both gases in PIL (Figure 4). Figure 5 also demonstrates that the IL solubility occurs in the order $CO_2 > CH_4 > N_2$, whilst in the PIL a different order is obtained $CO_2 > N_2 > CH_4$.

The composite membranes of PIL–IL are blends, combining the CO_2 separation properties of the PIL and that of the IL. The permeability of all gases increases dramatically in PIL-IL composites when compared to the pure polymer. The addition of only 20 wt% of IL increases CO_2, CH_4 and N_2 permeabilities 391%,

444% and 239%, respectively while, for the PIL–60 IL membrane, permeability enhancements of roughly 3829%, 7011% and 2970% occurred. These increased permeabilities can be attributed to quicker gas diffusion through the membranes with free IL (Figure 4). Moreover, a comparison between Figures 4 and 5 shows higher increments in gas diffusivity than in the gas solubility of the composite membranes. The diffusivity of all gases in PIL–IL composites increases with the concentration of IL incorporated into the membrane (Figure 4), probably due to the enhancement of polymer chain mobility and consequently a lower resistance to gas diffusion created by the free ions pairs. Conversely, the opposite behavior occurs in permeability (Table 2) and diffusivity (Figure 4) when the polymerizable component is added to IL (PIL–80 IL).

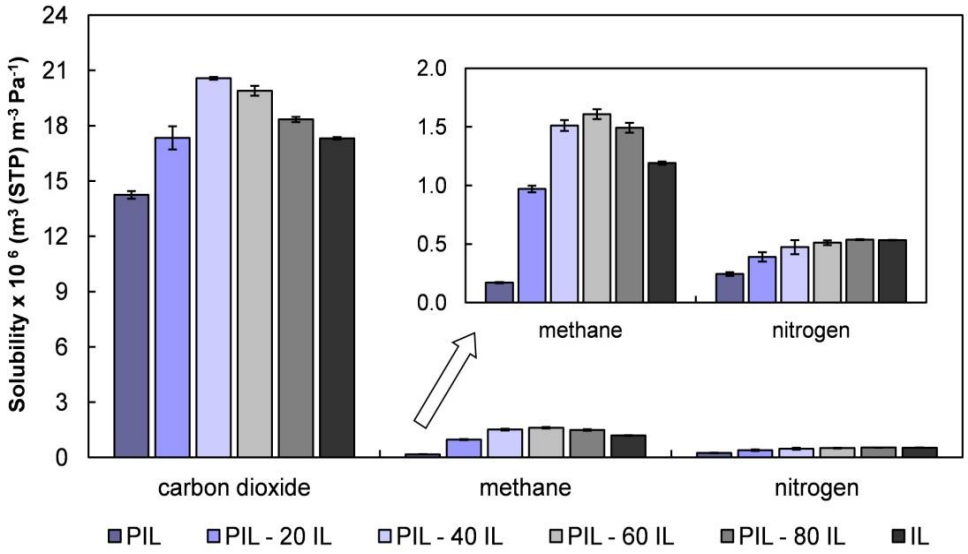

Figure 5| Gas solubility in pyrrolidinium-based membranes, calculated using Equation (4).

The incorporation of IL into PIL promotes a permselectivity increase of 44%, 36% and 27% for CO_2/N_2 in PIL–20 IL, PIL–40 IL and PIL–60 IL, respectively. In contrast, the CO_2/CH_4 permselectivity decreases 12%, 53% and 82% for the same composites (Table 2). Figure 6 also shows that the high level of CO_2/CH_4 solubility

selectivity of pure PIL is not present in the composite membranes possibly due to the presence of IL, since the solubility of CH_4 is much larger in IL than in the pure PIL (Figure 5). On the other hand, since the permselectivity of CO_2/N_2 in the PIL is lower than that obtained for pure IL (Table 2), the presence of IL in the composite membrane promotes the enhancement of CO_2/N_2 separation. It is worthwhile mentioning that for PIL–20 IL and PIL–40 IL the obtained CO_2/N_2 permselectivity is higher than that of both pure PIL and IL and, thus, an unexpected synergistic effect was observed. Additionally, when compared to CO_2/CH_4 separation, the improvement of CO_2/N_2 in PIL–IL membranes can also be attributed to the higher solubility selectivity between the two gases (Figure 6) and to the faster diffusivity of N_2 compared to CH_4 (Figure 4).

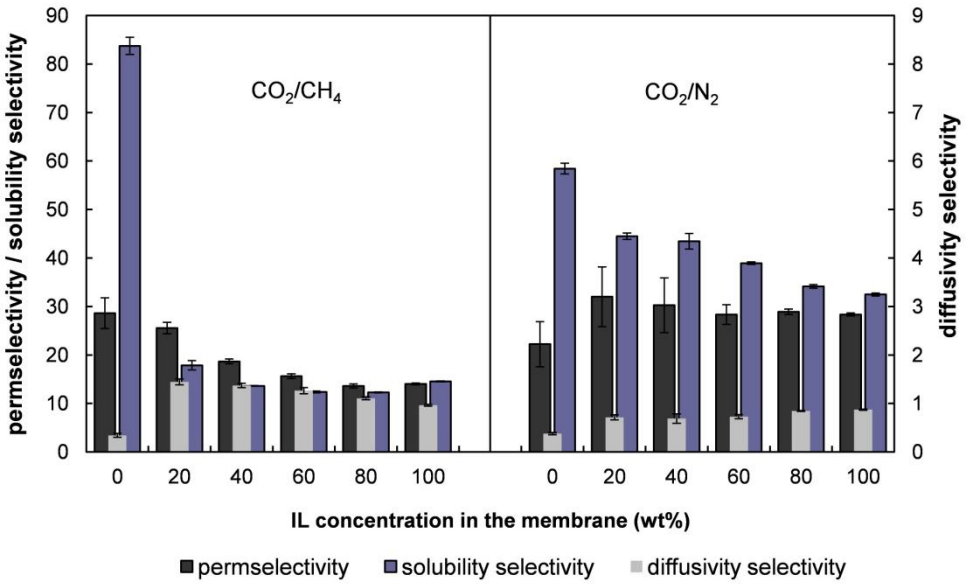

Figure 6| Permselectivity, solubility selectivity and diffusivity selectivity of CO_2/N_2 and CO_2/CH_4 of the pyrrolidinium-based membranes.

4.2. CO_2 separation performance

The comparison of CO_2/CH_4 and CO_2/N_2 separation efficiencies between the results obtained in this work and the previously published data for other membranes based on ionic liquids can be seen in Figure 7(a) and Figure 7(b), respectively, in the form of "Robeson Plots".[56] These plots are useful for showing the performance of a membrane given a particular separation and are widely used for illustrating the progress in membrane science for gas separation.[32, 56] The upper bound of a Robeson Plot is based on large amounts of experimental data for each separation and represents the current permselectivity limit for gas permeability vs. permselectivity for known polymeric gas separation membranes.[56]

Our experimental data plus three sets of data are depicted in Figure 7. One group represents polymeric ionic liquid membranes; the second are supported ionic liquid membranes; and the third group PIL–IL composite membranes based on the imidazolium cation with just 20 wt% of IL. The pure materials tested for the first time, poly([pyr_{11}][NTf_2]) and [C_4mpyr][NTf_2], do not outperform any imidazolium-based polymeric ionic liquid or supported ionic liquid membrane, respectively, previously tested for CO_2/CH_4 and CO_2/N_2 separations (Figure 7). Actually, their performances fall within the general range of published data for each case.[25, 26, 31, 37-39, 42, 57] Nevertheless, a direct comparison between the PIL made up of a pyrrolidinium cation instead of an imidazolium cannot be made because of differences in the structure of the polymer backbone. For instance, the functionality of most of the PILs based on imidazolium tested for CO_2 separation membranes exists as a pendant side group linked to a hydrocarbon backbone,[35, 37, 38, 45, 54] and poly([pyr_{11}][NTf_2]) has the pyrrolidinium functionality in the polymer main-chain (Figure 1).

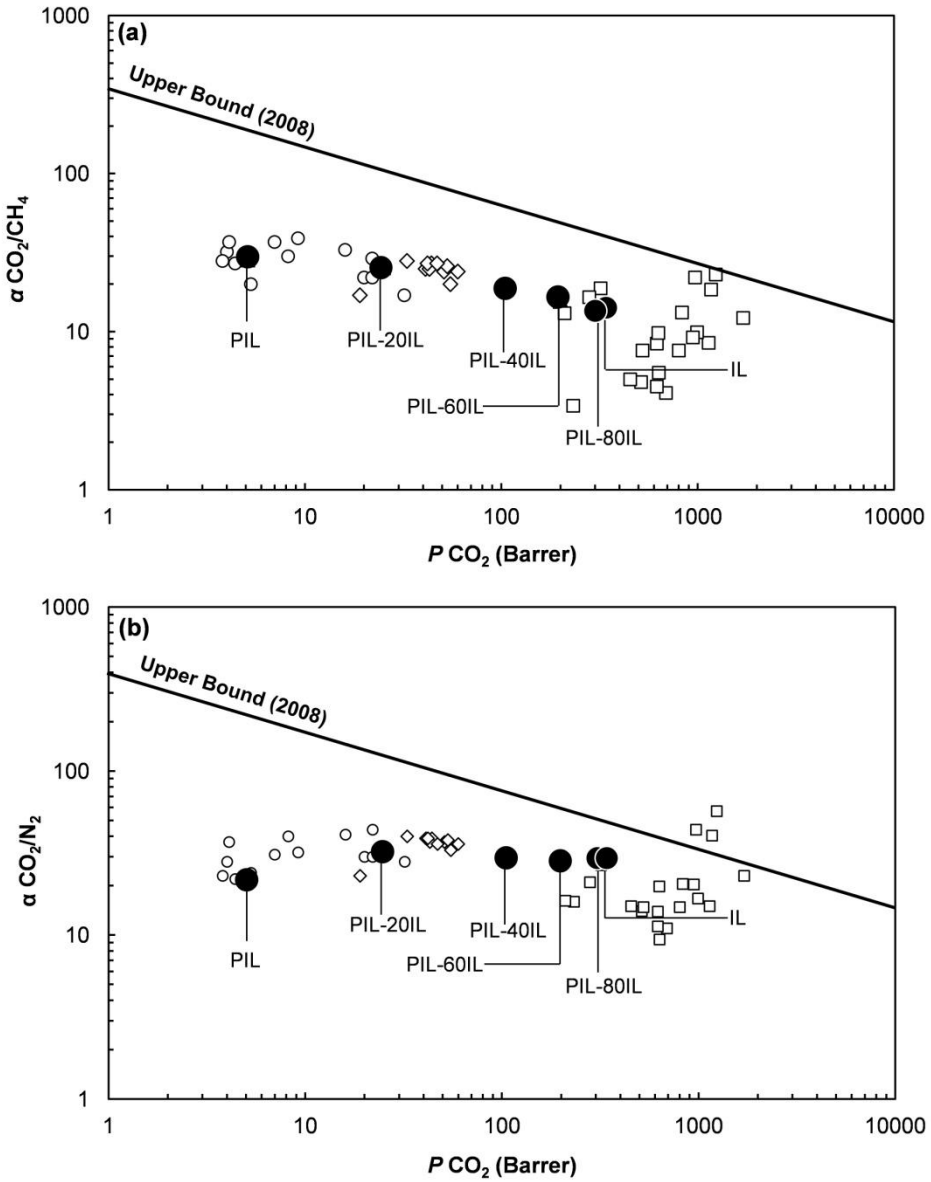

Figure 7| Robeson plots of the studied gases in prepared membranes. Data are plotted on a log-log scale and the upper bound is adapted from Robeson.[56] (a) CO_2/CH_4 permselectivity vs. CO_2 permeability and (b) CO_2/N_2 permselectivity vs. CO_2 permeability of all pyrrolidinium-based membranes prepared (●). Also plotted in (a) and (b) are other polymeric ionic liquid membranes (○),[37-39, 42] supported ionic liquid membranes (□),[25, 26, 31, 57] and polymeric ionic liquid composite membranes (◊).[40-42, 44]

The whole material range performance, from pure PIL to pure IL passing through their composites, can be clearly seen in Figure 7. The permselectivity of the PIL–20 IL composite membrane is in the same Robeson Plot region of other reported composite membranes based on imidazolium with 20 wt% of IL.[40-42, 44] However, PIL–40 IL, PIL–60 IL, PIL–80 IL composites fill the gap between those reported for other PIL–20 IL composites and supported ionic liquid membranes (Figure 7). Consequently, these prepared membranes serve as link to understanding the behavior and show the CO_2 separation performance of the whole material range. It is also clear that the permeability influence of adding free IL into the PIL is much greater than the addition of PIL into the IL. This means that the incorporation of only 20 wt% of IL into PIL causes a dramatic shift of the results along the *x*-axis change. In contrast, when 20 wt% of the polymerizable material is added to IL a very small change in CO_2 permeability is observed.

The Robeson plots also indicate that CO_2/N_2 (Figure 7(b)) is a more favorable separation than CO_2/CH_4 (Figure 7(a)) for the PIL–IL composite membranes herein prepared. As discussed above, the addition of IL increases the CO_2/N_2 and decreases CO_2/CH_4 permselectivity of the resulting PIL-IL composite membranes, mainly due to the intrinsic permselectivity properties of the IL incorporated for each gas pair. Moreover, the performance of pyrrolidinium-based composite membranes is still below the upper bound (from 2008) for both separations CO_2/N_2 and CO_2/CH_4 and comparable with studies using other PIL membranes. In fact, it should be possible to improve the CO_2 separation performance of the pyrrolidinium-based membranes by using different ILs with higher CO_2/CH_4 and/or CO_2/N_2 permselectivity properties. Our results demonstrate that the IL properties have a great impact on the CO_2 separation performance of PIL–IL membranes. Consequently, the IL choice is crucial in the tailoring of the PIL–IL membrane properties for improving their CO_2 separation performance.

5. Conclusions

Permeability, solubility and diffusivity of CO_2, N_2, and CH_4 in a new series of polymeric ionic liquids composite membranes based on poly([pyr_{11}][NTf_2]) by the addition of 0, 20, 40, 60, 80 and 100 wt% of [C_4mpyr][NTf_2] were measured using a time-lag apparatus. Results showed that PIL–IL composites are very promising materials for gas separation membranes since their properties can be highly tuned by the incorporation of free IL.

The study of the full material range allows for the selection of the appropriate amount of IL so that the gas separation composite membrane closest to the upper bound of the Robeson plot can be prepared. Also, the analysis of the whole material range elucidates the role of the IL in permeation properties of the composite. The permselectivity/permeability properties of the poly([pyr_{11}][NTf_2]) are of the same order of magnitude as those of imidazolium-based polymers also containing $[NTf_2]^-$ anion. The presence of free IL into poly([pyr_{11}][NTf_2]) promotes the enhancement of CO_2/N_2 permselectivity in the composite membranes. In contrast, their CO_2/CH_4 permselectivity decreases. Nevertheless, composite membranes with finest CO_2/N_2 separation performances were obtained by the incorporation of 20 and 40 wt% of free IL, which promoted a CO_2/N_2 permselectivity increase of 44% and 36%, respectively, with respect to the pure polymer ionic liquid membrane. It is worthwhile mentioning that for these composite membranes the obtained CO_2/N_2 permselectivity is higher than that of both pure PIL and pure IL and, thus, surprising improvements of the CO_2/N_2 separation performance were obtained.

Concluding, the results for the two different gas separations studied, CO_2/N_2 and CO_2/CH_4, indicate that the IL permeability properties greatly influence the properties of the composite membranes. It is, thus, possible to choose an ionic liquid with appropriate properties for a desired separation.

6. Acknowledgements

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Chapter 6

Polymeric ionic liquids with mixtures of counter-anions for CO_2 separation

Adapted from: **L.C. Tomé,** M.A. Aboudzadeh, L.P.N. Rebelo, C.S.R. Freire D. Mecerreyes, I.M. Marrucho, Polymeric ionic liquids with mixtures of counter-anions: a new straightforward strategy for designing pyrrolidinium-based CO_2 separation membranes, *J. Mater. Chem. A,* 2013, **1**, 10403-10411.

The author contributed to the planning and execution of all the experiments presented herein, as well as on the discussion, interpretation and preparation of the manuscript. The TGA and FTIR analyses were performed by M.A. Aboudzadeh.

1. Abstract

Polymeric ionic liquids (PILs) are interesting membrane materials for CO_2 separation. In order to increase the flexibility in tailoring the permeability and selectivity of PIL-based membranes for flue gas separation and natural gas purification, this work explores the use of PILs with mixtures of counter-anions employing a straightforward strategy. A new family of PIL random copolymers having pyrrolidinium cation pendant units combined with different counter-anion mixtures was synthesized and characterized. A simple and quantitative anion exchange procedure was successfully applied to the commercially available poly(diallyldimethylammonium) chloride as confirmed by NMR, FTIR and titration experiments. Composite membranes of the copolymers with 20 wt% of free ionic liquid ($[C_4mpyr][NTf_2]$) were prepared and their CO_2, CH_4, and N_2 permeation properties were measured. In addition, their tensile mechanical properties were also assessed. The results show that the permeability of all gases in the composite membranes is related to their gas diffusivities which are strongly dependent on the second counter-anion. The prepared membranes exhibit permselectivities ranging from 10.8 to 29.3 for CO_2/CH_4 and from 21.4 to 32.0 for CO_2/N_2. Furthermore, their CO_2 separation performance as a function of permeability can be tuned by using PILs with different counter-anions mixtures, which opens new possibilities for designing the CO_2 separation of these materials.

2. Introduction

Development of economically and sustainable CO_2 capture processes is becoming increasingly important as concerns on rising anthropogenic CO_2 levels, leading to global warming and unpredictable climate changes, are being widely expressed. Therefore, the design of materials with the ability to efficiently separate CO_2 from other gases is of vital importance.

Ionic liquids (ILs), widely promoted as "designable" solvents, have been blossoming at the interface of many branches of chemistry.[1] ILs are low-melting-point salts and, apart from their broad definition as compounds with a unique combination of properties such as negligible volatility,[2] thermal stability,[3] low flammability,[4] and high ion conductivity,[5] their most attractive feature is their tunability making these liquids absolutely unique and incomparable to other solvents. Owing to their remarkable CO_2 solubility and selectivity relative to CH_4 and N_2,[6] ILs have been explored as possible alternative media for CO_2 separation,[7, 8] particularly in applications involving membrane technology. In this context, a large range of different ILs has been tested in combination with porous membranes as supported ionic liquid membranes.[9-19] Nevertheless, it has been shown that the best way to approach ILs for CO_2 separation using membranes is to polymerize the ionic liquid monomers and prepare solid polymer membranes in order to overcome the pressure stability issue inherent to supported ionic liquid membranes.[20]

In the past few years, polymeric ionic liquids have aroused strong interest since they combine some of the exceptional and unique properties of ILs with the macromolecular architecture and improved mechanical stability of polymers.[21-26] Although pioneering studies anticipated the use of PILs as advanced polymer electrolytes,[27-30] this new class of functional polymers has also been proposed as CO_2 sorbent materials.[31-34] Shen *et al.* first reported the study of CO_2 absorption by imidazolium-based PILs combining tetrafluoroborate ($[BF_4]^-$) and hexaflourophosphate ($[PF_6]^-$) anions. These authors showed that those PILs exhibited even higher CO_2 absorption capacity and faster absorption/desorption rates than the corresponding ionic liquids.[31] It has also observed that the CO_2 sorption properties of pyrrolidinium-based PILs are significantly affected by the nature of the counter-anion.[33] Furthermore, Noble *et al.* established the potential of PILs as promising materials for membrane-based CO_2 separations with CO_2/CH_4

and CO_2/N_2 permeability selectivities on par or greater than those observed for conventional supported ionic liquid membranes.[35-37] Even though PILs afford solid stable membranes, their major drawback is the substantial drop in both gas permeability and diffusivity when compared to their analogous liquid phase in supported ionic liquid membranes. Therefore, different approaches have been explored for increasing gas permeability and diffusivity in PILs, including the blending of free ILs with PILs to form homogeneous composite membranes,[38-42] the incorporation of nanofillers into PILs to obtain mixed matrix membranes,[43, 44] and the use of cross-linked PILs to prepare gel membranes containing large amounts of free IL.[45-47] Despite all the progress, the efforts in the use of PILs as CO_2 separation membranes mostly used imidazolium moieties as pendent groups of the polymer backbone combined with the bis(trifluoromethylsulfonyl)imide anion ($[NTf_2]^-$).[35-41, 43-46] The published data for PILs not only show promising CO_2 separation factors but also the lack of diversity in what concerns the different chemical structures of cations and anions. On top of that, IL mixtures have been proposed as a mean to further increase flexibility and the fine-tune capacity of the physical-chemical as well as CO_2 solubility selectivity properties of these compounds.[48-50] Although this seems to be a promising strategy that provides an extra degree of freedom in the design of new materials, its exploitation using PIL-based membranes for CO_2 separation has never been attempted before.

In our previous work, we prepared a series of pyrrolidinium-based polymeric ionic liquid membranes combining the $[NTf_2]^-$ anion and showed that their permselectivity/permeability properties are of the same order of magnitude as those of imidazolium-based PILs also containing $[NTf_2]^-$ as anion.[51, 52] It is worthy to note that the pyrrolidinium-based PIL used was synthesized by carrying out the anion exchange directly into the commercially available poly(diallyldimethylammonium) chloride.[53] This synthetic route is clearly less complicated than that used to prepare the commonly used imidazolium-based

PILs, which involve a number of organic syntheses and purification steps at the monomer level as well as the need to control polymerization conditions. What is more, pyrrolidinium-based PILs have been proven to be more environmental-friendly that the commonly used imidazolium.[54]

All the above mentioned aspects motivated us to explore new possibilities of designing CO_2 separation membranes based on pyrrolidinium ionic materials. In the present work, we report the synthesis and characterization of new PIL random copolymers having a pyrrolidinium functionality combined with different counter-anion mixtures which were obtained by straightforward and efficient anion exchange reactions directly from the cheaply available chloride polymer. The anions used were chosen based on their hydrophobic nature and the commercial availability of their respective salts. Since the membranes of the pure pyrrolidinium random copolymers were brittle and broke during the experiments, composites membranes of the copolymers with 20 wt% of free IL were prepared and both their mechanical properties and their CO_2, CH_4, and N_2 permeation properties were evaluated and presented.

3. Experimental Section

3.1. Materials

Poly(diallyldimethylammonium) chloride solution (average Mw 400 000–500 000, 20 wt% in H_2O), potassium hexafluorophosphate (KPF_6, 98%), sodium dodecylbenzenesulfonate (NaDBSA), sodium 2-naphthalenesulfonate (NaNSA, ≥ 95%) and sodium dodecyl sulfate (NaDS, ≥ 98.5%) were purchased from Sigma-Aldrich. Lithium bis(trifluoromethylsulfonyl)imide ($LiNTf_2$, 99.9%) was provided by Solvionic. 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ($[C_4mpyr][NTf_2]$) (99 wt% pure) was supplied by IoLiTec GmbH. All the other solvents were of analytical grade and used as received. CO_2, N_2, and CH_4 were

supplied by Air Liquide and were of at least 99.99% purity.

3.2. Synthesis of pyrrolidinium random copolymers

Poly(diallyldimethylammonium)bis(trifluoromethylsulfonyl)imide ($PIL(NTf_2)$) containing pyrrolidinium pendant units with only NTf_2 as counter-anion was synthesized by an anion exchange reaction from the commercially available pyrrolidinium-based polymer, poly(diallyldimethylammonium) chloride, according to a procedure described elsewhere.[53] In a typical procedure, to prepare poly(diallyldimethylammonium) bis(trifluoromethylsulfonyl)imide hexafluorophosphate ($PIL(NTf_2/PF_6)$), a solution of both salts, $LiNTf_2$ (5.33 g, 18.6 mmol) and KPF_6 (3.42 g, 18.6 mmol) in 10 mL of distilled water, and a solution of poly(diallyldimethylammonium) chloride (6 g, 37.1 mmol of monomeric units) in 150 mL of distilled water were mixed in a round bottom flask by stirring for 10 min at room temperature. Poly(dialyldimethylammonium) bis(trifluoromethylsulfonyl)imide 2-naphthalenesulfonate ($PIL(NTf_2/NSA)$), poly(dialyldimethylammonium) bis(trifluoromethylsulfonyl)imide dodecyl sulfate ($PIL(NTf_2/DS)$) and poly(dialyldimethylammonium) bis(trifluoromethylsulfonyl)imide dodecylbenzenesulfonate ($PIL(NTf_2/DBSA)$) were also obtained following the same procedure as for $PIL(NTf_2/PF_6)$. In all the cases, the new formed pyrrolidinium random copolymers became hydrophobic and precipitate quantitatively in the aqueous media. Then, the obtained solids were washed with water, filtered and dried until constant weight was attained.

3.3. Polymer characterization

The pyrrolidinium random copolymers synthesized in this work were characterized by ^1H- and ^{13}C-NMR spectroscopy, infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). The CO_2 separation performance and the

mechanical properties of the prepared composite membranes were evaluated using gas permeation measurements and tensile tests, respectively.

^{1}H- and ^{13}C-NMR spectra were recorded with a Bruker AC-500 spectrometer. The samples were dissolved in appropriate deuterated solvents.

FTIR spectra were acquired using a Bruker ALPHA spectrometer. The resolution was 4 cm^{-1} after 42 scans. Spectra were collected from 4000 to 250cm^{-1}.

Thermogravimetric analysis were carried out using a TGA 2950/Q500 analyzer. Samples were heated at a constant rate of 10 K min^{-1}, from room temperature to 923 K, under nitrogen atmosphere. The thermal decomposition temperature was taken as the onset of significant (~0.5%) weight loss, after the initial moisture loss.

Tensile tests were performed at 294 K under 41% of relative humidity on a TA-Hdi Stable Micro Systems Texture Analyser using a load cell of 5 Kg and operating at a deformation rate of 0.5 mm s^{-1}. Tensile modulus, tensile strength and elongation at break were calculated using the Instron Series IX software.

3.4. Preparation of composite membranes

Free standing composite membranes based on the synthesized pyrrolidinium random copolymers with free ionic liquid were prepared by a solvent casting method. Initially, 12% (w/v) solutions of each polymer in appropriate solvents were prepared and [C_4mpyr][NTf_2] was added in order to obtain solutions with 20 wt% of free IL to the polymer matrix. The solutions were magnetically stirred for 12 hours. Afterwards, transparent and free standing membranes were obtained by casting each solution into Petri dishes. The experimental conditions of the solvent casting process for each composite membrane are present in Table 1. All solvents were slowly evaporated in a saturated solvent environment in order to obtain homogeneous membranes. Finally, all the membranes were dried in an oven (373 K) until a constant weight was observed. Membrane thicknesses (120 –

145 µm) were measured using a digital micrometer (Mitutoyo, model MDE-25PJ, Japan). The prepared free standing composite membranes exhibited no evidence of phase separation between the polymer and the ionic liquid components, even after storing at ambient conditions for several months.

3.5. Gas permeation measurements

Single gas permeabilities and diffusivities through the prepared composite membranes were measured using a time-lag apparatus. Details on the construction and operation of this experimental setup are entirely described elsewhere.[52] All the membranes were degassed under vacuum inside the permeation cell during 24 hours before testing. The single gas permeation experiments using CO_2, CH_4, and N_2 were performed at 293 K with a trans-membrane driving force of 100 kPa upstream against initial vacuum downstream (<0.1 kPa). At least three separate experiments of each gas on a membrane sample were performed. Between experiments, the membrane sample was degassed under dynamic vacuum until the downstream pressure was below 0.1 kPa. The membrane thickness was measured before and after testing. Average thickness was calculated from six measurements taken at different locations of each membrane sample. No residual ionic liquid was found inside the permeation cell at the end of the experiments and, similarly, the composite membrane mass remained constant throughout the experiment.

The gas transport through a dense polymer membrane occurs according a solution-diffusion mass transfer mechanism where the permeability (*P*) is related to solubility (*S*) and diffusivity (*D*) as follows:[55]

$$P = S \times D \tag{1}$$

Permeability (*P*) is defined as the steady-state gas flux (*J*) through a membrane under a transmembrane pressure drop (Δ*p*) and normalized to the unit thickness of the membrane as follows:[56]

$$P = J\frac{\ell}{\Delta p} \tag{2}$$

The flux was determined experimentally using Equation 3, where V^p is the permeate volume, Δp_d is the variation of downstream pressure, *A* is the effective membrane surface area, *t* is the experimental time, *R* is the Ideal Gas Law constant and *T* is the absolute temperature.

$$J = \frac{V^p \Delta p_d}{AtRT} \tag{3}$$

Diffusivity (*D*) was obtained according to Equation 4. The time-lag parameter (θ), which can be obtained before achieving steady-state flux, was deduced by extrapolating the slope of the linear portion of the p_d vs. *t* curve back to the time axis, where the intercept is equal to θ.[57]

$$D = \frac{\ell^2}{6\theta} \tag{4}$$

After knowing both *P* and *D*, it was also possible to calculate *S* using the relationship shown in Equation (1).

The ideal permeability selectivity (or permselectivity), $\alpha_{i/j}$, was obtained by dividing the permeability of the more permeable specie *i* to the permeability of the less permeable specie *j*. As shown in Equation (5), the permselectivity can also be expressed as the product of the diffusivity selectivity and the solubility selectivity.

$$\alpha_{i/j} = \frac{P_i}{P_j} = \left(\frac{D_i}{D_j}\right) \times \left(\frac{S_i}{S_j}\right) \tag{5}$$

4. Results and Discussion

4.1. Synthesis and characterization of pyrrolidinium-based polymers

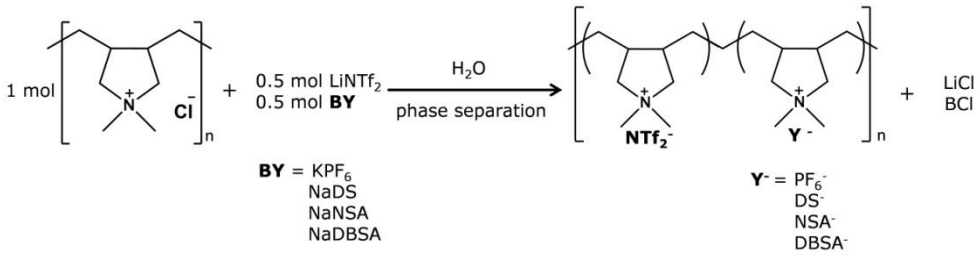
Generally, PILs can be synthesized via two routes: the first one consists on synthesizing monomers with the desired anions and then different PILs are obtained by direct polymerization of each IL monomer,[27, 28, 30, 58, 59] while the second route consists on carrying out the anion exchange reaction directly into the water soluble polycation containing an halide anion.[60-63] Depending on the targeted PIL both methods can comprise some advantages and/or disadvantages.[23, 24]

Concerning to pyrrolidinium-based PILs, homopolymers were already synthesized by both synthetic routes,[33, 53] whereas copolymers were only prepared using the first route involving the polymerization of IL monomers.[64] However, several organic syntheses and purification steps at the monomer level are required, as well as the need of controlling the polymerization conditions of each individual co-monomer. The second route is undoubtedly less complicated as it involves only one synthetic step from the commercially available poly(diallyldimethylammonium) chloride, although no further chemical modification of the polypyrrolidinium backbone are possible.[65]

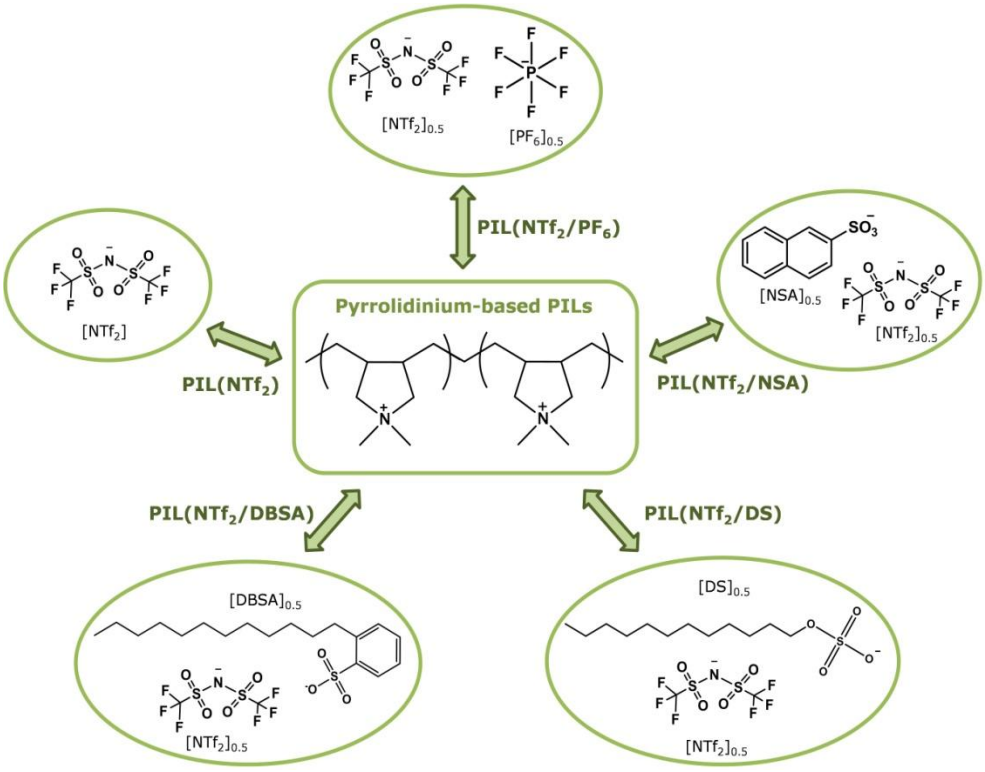
To the best of our knowledge, this is the first time that the synthesis of pyrrolidinium random copolymers via the second synthetic strategy is attempted. Indeed, a clear advantage of using this strategy throughout our studies is the increased possibility to design new pyrrolidinium random copolymers with counter-anion mixtures solely by straightforward salt metathesis reactions, directly from the same initial polymer where afterwards only a simple purification step by filtration is required.

Scheme 1 shows the synthetic procedure of the pyrrolidinium random copolymers which consists on carrying out the simple anion exchange reactions

into the water soluble poly(diallyldimethylammonium) chloride using mixtures of different salts. As a result, the pyrrolidinium random copolymers precipitated quantitatively in water and were recovered by filtration. The chemical structures of the synthesized pyrrolidinium-based PILs are shown in Scheme 2.



Scheme 1| Anion exchange reactions proposed for the synthesis of the pyrrolidinium random copolymers.



Scheme 2| Chemical structures of the pyrrolidinium-based PILs.

The chemical nature of the copolymers was confirmed by NMR and FTIR spectroscopy. ^{1}H- and ^{13}C-NMR spectra (not shown) of all the synthesized copolymers confirmed the nature of the pyrrolidinium backbone, poly(diallyldimethylammonium).[53]

The FTIR spectra of the copolymers reveal the presence of the different counter-anions. As it can be seen in Figure 1, the absorption bands attributed to the $[NTf_2]^-$ anion at 1337, 1172, 1135 and 1045 cm^{-1} are clearly observed in all the spectra, since this counter-anion is common in all the copolymers. The new absorption bands related with the second counter-anion appear as follows: at 839 cm^{-1} associated with the $[PF_6]^-$ absorption in the spectrum of PIL (NTF_2/PF_6); at 1035 and 662 cm^{-1} in the PIL (NTf_2/NSA); and at 2923, 2847 and 977 cm^{-1} in the case of PIL (NTf_2/DS). Titration tests, which consist on the addition of $AgNO_3$ (1 g) to appropriate solvent solution of each polymer, were also carried out. All the tests were negative, confirming that no chloride counter-anions remained in the PILs since no precipitation of AgCl occurred.

In Figure 2 the TGA profiles of the different PILs containing the counter-anion mixtures are presented. The thermal stability of the copolymers shows intermediate behaviors to that of both the corresponding homopolymers. In our case, the copolymers showed decreased thermal stability as compared with the thermally stable PIL (NTf_2) in the order PIL (NTf_2/DS) < PIL (NTf_2/PF_6) < PIL (NTf_2/NSA) < PIL (NTf_2/DBSA), which is in agreement with the observed thermal stability of the respective PIL homopolymers.[53] These results in combination with the NMR, FTIR and the silver titration observations confirmed that the anion exchange reactions were quantitative.

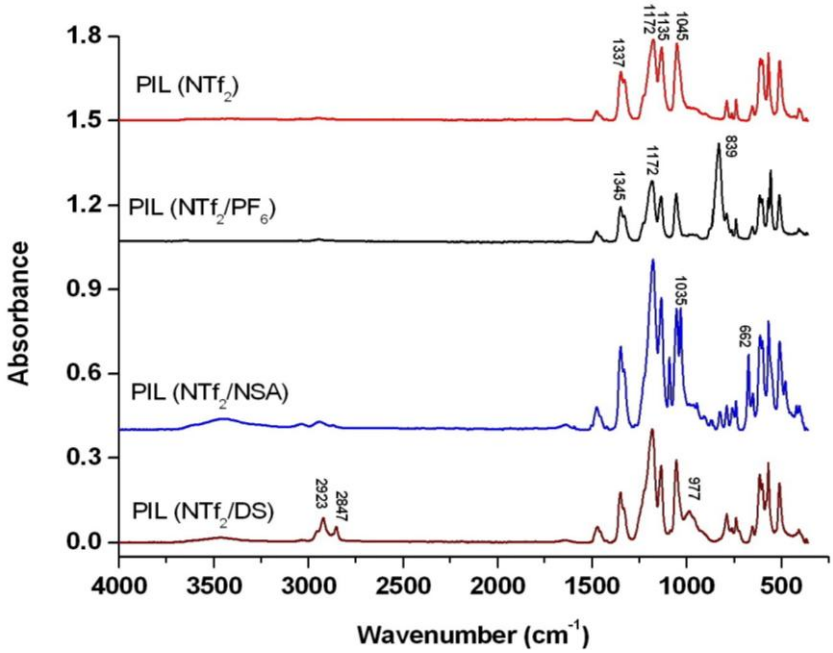


Figure 1| FTIR transmission spectra of the pyrrolidinium-based PILs containing different counter-anion mixtures.

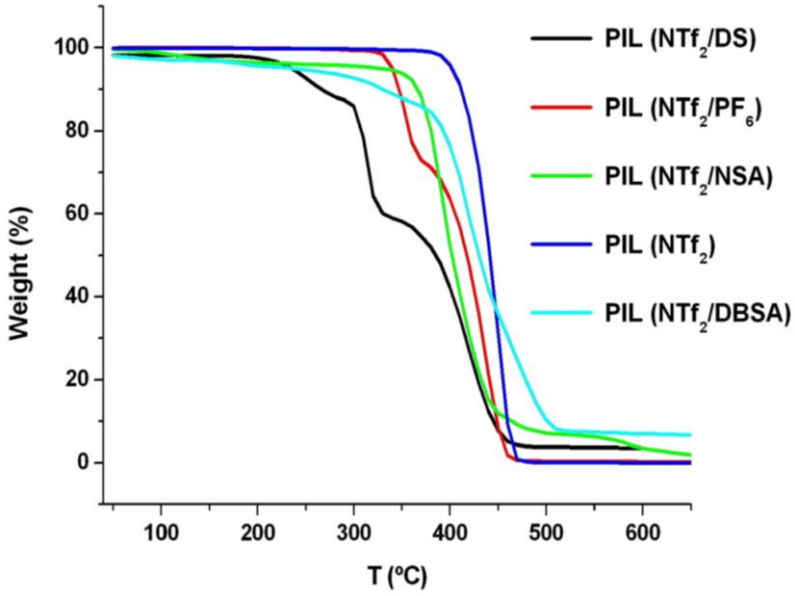


Figure 2| TGA profiles of the pyrrolidinium-based PILs containing different counter-anion mixtures.

4.2. Gas permeability, diffusivity and solubility

Composite membranes of pyrrolidinium random copolymers with 20 wt% of free IL were prepared (Table 1), because the pure copolymers were brittle and broke during the gas permeation experiments. It should be pointed out that the addition of free IL into PILs drastically increase the CO_2 permeability and diffusivity while maintain the CO_2 selectivity of the composite membranes.[38-40] All the prepared composite membranes were homogeneous and exhibited no evidence of phase separation even after several months of storage at ambient conditions.

Table 1| Composition descriptions and experimental conditions of the casting procedure (solvent, temperature and time of solvent evaporation) used to prepare each composite membrane studied.

Membrane sample	Polymer	20 wt% of IL	Solvent	T (K)	Time (days)
PIL (NTf_2)–20IL	PIL (NTf_2)	[C_4mpyr][NTf_2]	Acetone	298	1
PIL (NTf_2/PF_6)–20IL	PIL (NTf_2/PF_6)	[C_4mpyr][NTf_2]	Acetonitrile	303	2
PIL (NTf_2/NSA)–20IL	PIL (NTf_2/NSA)	[C_4mpyr][NTf_2]	DMSO	353	3
PIL (NTf_2/DS)–20IL	PIL (NTf_2/DS)	[C_4mpyr][NTf_2]	DMF	338	2
PIL (NTf_2/DBSA)–20IL	PIL (NTf_2/DBSA)	[C_4mpyr][NTf_2]	DMSO	353	3

The measured gas permeability and diffusivity values in the composite membranes of the pyrrolidinium random copolymers with 20 wt% of free IL are shown in Figure 3(a) and Figure 3(b), respectively, while the gas solubility values calculated using Equation (1) are presented in Figure 3(c).

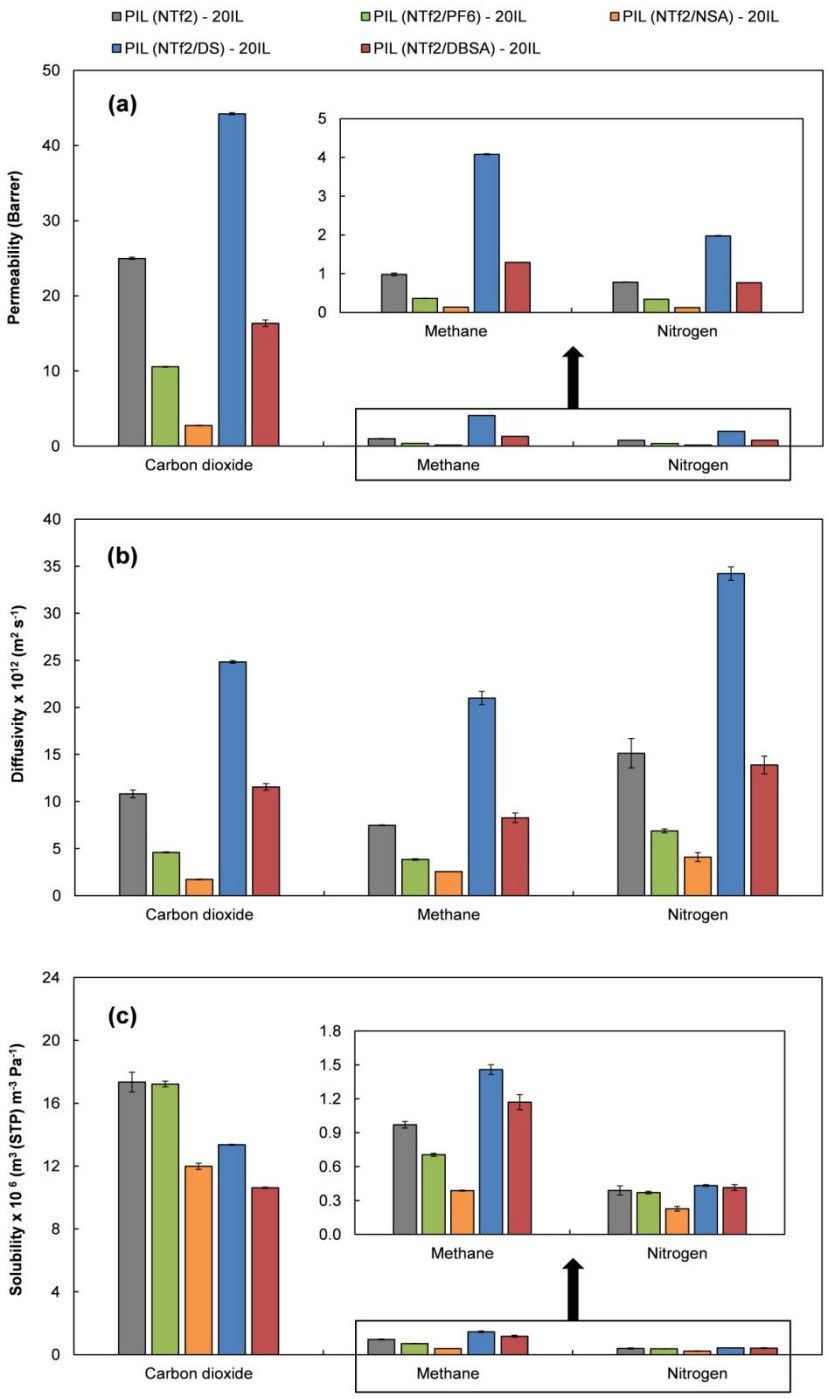


Figure 3| Gas (a) permeability, (b) diffusivity and (c) solubility in the prepared composite membranes. Error bars represent standard deviations based on three experimental replicas.

The CO_2 permeability values vary from 3 to 25 Barrer, while CH_4 and N_2 permeabilities differ from 0.12 to 4.08 Barrer. The same trend obtained for the permeability between gases (P CO_2 >> P CH_4 > P N_2), was also observed for the solubility (S CO_2 >> S CH_4 > S N_2) of all the composites. Although the gas molecules dissolve into the membrane and diffuse through it, the differences between the permeability of gases mainly arise from the solubility differences of each gas component. Therefore, the high CO_2 permeability compared to that of CH_4 and N_2 (Figure 3(a)) can be essentially attributed to the high levels of CO_2 solubility relative to CH_4 and N_2 (Figure 3(c)).

The results presented in Figure 3(a) also show that the membranes containing the pyrrolidinium random copolymers and 20 wt% of free IL posses gas permeabilities that were substantially different than that of PIL (NTf_2)–20IL. It is possible to observe that the relative gas permeability reduction or enhancement is strongly dependent on the second counter-anion. For instance, the presence of the DS counter-anion in the PIL (NTf_2/DS)–20IL composite membrane increases the CO_2, CH_4 and N_2 permeabilities by 76%, 316% and 153%, respectively, compared to those of the PIL (NTf_2)–20IL. In contrast, the NSA counter-anion decreases 733%, 654% and 550% the CO_2, CH_4 and N_2 permeabilities, respectively.

We note that diffusivity is the primary factor differentiating CO_2, CH_4 and N_2 permeabilities in the PIL (NTf_2)–20IL from that of the composite membranes comprising the PIL copolymers with counter-anion mixtures. As it can be seen in Figure 3, the permeability of all gases in the composite membranes is related to their respective gas diffusivities, with the series from the highest to the lowest permeabilities (Figure 3(a)) being equal to that of diffusivities (Figure 3(b)): PIL (NTf_2/DS)–20IL > PIL (NTf_2)–20IL > PIL (NTf_2/DBSA)–20IL > PIL (NTf_2/PF_6)–20IL > PIL (NTf_2/NSA)–20IL. These data suggest that PIL (NTf_2/NSA) possesses a much glassier or rigid polymer matrix that inhibits gas diffusion through the PIL (NTf_2/NSA)–20IL composite membrane. The lower gas diffusion in the

PIL(NTf_2/PF_6)–20IL when compared to that of PIL(NTf_2)–20IL is probably due to the fact that $[PF_6]^-$ counter-anion is less flexible than the $[NTf_2]^-$ and thus contributes to a more packed polymer structure. Conversely, the highest gas solubilities and diffusivities obtained in the PIL (NTf_2/DS)–20IL can be attributed to the long aliphatic chain of the $[DS]^-$ counter-anion since their inefficient packing probably creates more free volume within the polymer network and consequently lower resistant to gas diffusion. Although the $[DBSA]^-$ counter-anion has also a long aliphatic chain (Scheme 2), the presence of the aromatic ring appears to promote a less effective polymer chain packaging than the $[DS]^-$ bulkier counter-anion, thus allowing for lower gas diffusivity in the PIL (NTf_2/DBSA)–20IL than that in PIL (NTf_2/DS)–20IL. Therefore, our results demonstrate that is possible to adjust and design the gas permeation properties of the composite membranes by incorporating into the pyrrolidinium-based PIL a second counter-anion with a different chemical structure.

4.3. CO_2 separation performance

The measured CO_2 permeabilities and both the CO_2/CH_4 and CO_2/N_2 permselectivities of the studied composite membranes are summarized in Table 2. These results are also plotted on the so-called Robeson Plots,[66] where the permselectivity between CO_2 and CH_4 (or N_2) is represented versus the CO_2 permeability (Figure 4). The upper bond of a Robeson Plot is based on large amount of experimental data for each separation and shows the tradeoff between permeability and permselectivity that has been observed for polymers and thus corresponds to the gas separation performance limit of these materials.[66, 67]

The Robeson Plots indicate that CO_2/CH_4 (Figure 4(a)) is a less favorable separation than CO_2/N_2 (Figure 4(b)) for the composite membranes herein prepared. In fact, the CO_2/CH_4 permselectivity is always smaller than CO_2/N_2

permselectivity (Table 2) since the CH_4 permeability is greater than that of N_2 in all the studied composite membranes (Figure 3(a)). These results are in agreement with previous works on PIL membranes containing imidazolium polycation.[35, 36, 31-34, 53]

Table 2| Single CO_2 permeability (P)[a] and ideal permselectivity (α) obtained in the prepared composite membranes.[b]

Membrane sample	P CO_2	α CO_2/CH_4	α CO_2/N_2
PIL (NTf_2)–20IL	25.0 ± 0.16	25.5 ± 1.1	32.0 ± 0.3
PIL (NTf_2/PF_6)–20IL	10.6 ± 0.04	29.3 ± 0.6	31.0 ± 0.2
PIL (NTf_2/NSA)–20IL	2.74 ± 0.03	20.5 ± 0.7	22.4 ± 0.7
PIL (NTf_2/DS)–20IL	44.2 ± 0.15	10.8 ± 0.1	22.4 ± 0.2
PIL (NTf_2/DBSA)–20IL	16.4 ± 0.44	12.7 ± 0.4	21.4 ± 0.7

[a] Barrer (1 Barrer = 10^{-10} cm^3(STP)cm cm^{-2} s^{-1} $cmHg^{-1}$)

[b] Errors represent the standard deviations, based on three experiments.

From Figure 4 it can be also observed that the incorporation of the second counter-anion into the PIL structure has a great impact on the CO_2 separation performance of the composite membranes. For instance, the incorporation of the $[NSA]^-$ as second counter-anion not only reduces the CO_2 permeability but also decreases the CO_2/CH_4 and CO_2/N_2 permselectivities of the PIL (NTf_2/NSA)–20IL compared to PIL (NTf_2)–20IL. The presence of the $[DS]^-$ counter-anion increases the CO_2 permeability of the composite membrane, but it also promotes decreased CO_2/N_2 and CO_2/CH_4 permselectivities (Table 2). This behavior is in accordance with the well-known tradeoff between polymer membrane flux and selectivity, which means that improvements in membrane permeability are generally coupled with a loss in their permselectivities. Even though the CO_2/N_2 permselectivity remained relatively unchanged between PIL (NTf_2)–20IL and PIL (NTf_2/PF_6)–20IL membranes, enhanced CO_2/N_2 permselectivity was obtained in the PIL (NTf_2/PF_6)–20IL (Table 2). Indeed, the incorporation of $[PF_6]^-$ as second counter-anion did not

only affects the CO_2/N_2 diffusivity selectivity but also increased the CO_2/N_2 solubility selectivity the PIL (NTf_2/PF_6)–20IL compared to PIL (NTf_2)–20IL.

Overall, Figure 4 clearly shows that the CO_2 separation performance of the PIL-IL membranes as a function of the permeability can be tuned by using pyrrolidinium-based PILs containing different mixtures of counter-anions since the anion structure plays an important role on the gas transport properties through those membranes.

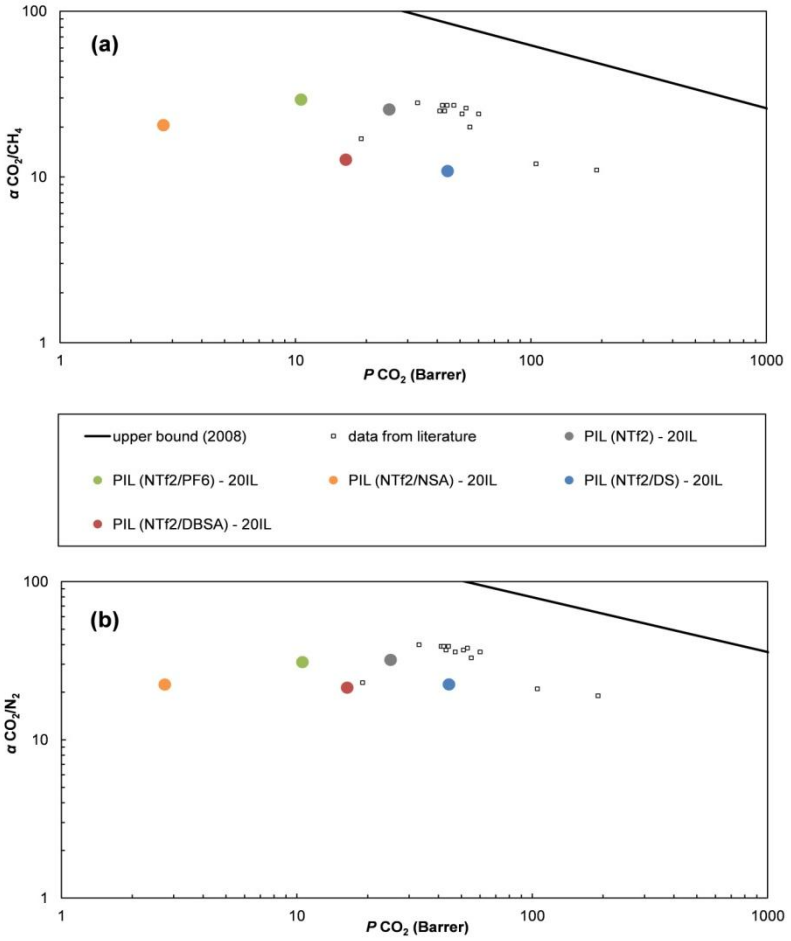


Figure 4| CO_2 separation performance of the studied composite membranes plotted on (a) CO_2/CH_4 and (b) CO_2/N_2 Robeson plots. Experimental error is within the data points. Data are plotted on a log-log scale and the upper bound for each gas pair is adapted from Robeson. [66] Literature data reported for other polymeric ionic liquid composite membranes combining 20 wt% of free ionic liquid are also plotted. [31-34, 53]

4.4. Mechanical properties

The large strain behavior of all the prepared composite membranes based on the pyrrolidinium random copolymer and 20 wt% of free IL was studied up to their failure. Figure 5 shows the tensile mechanical properties, including the Young modulus, tensile strength and elongation at breakage, determined from the typical stress–strain curves obtained. The contrast in the mechanical properties of the studied composite membranes is clearly visible. The PIL (NTf_2/NSA)–20IL, PIL (NTf_2/DS)–20IL and PIL (NTf_2/DBSA)–20IL membranes displayed quite low Young's moduli, tensile strengths and elongations at break, which is in agreement with the considerable fragility of these membranes. This behavior is probably associated with the introduction of the anions with long aliphatic chains and aromatic rings that certainly affected the way in which the polymeric chains interact and therefore their packing during the casting process. The PIL (NTf_2)–20IL and PIL (NTf_2/PF_6)–20IL membranes, composed only of fluorinated based counter-anions, showed the best mechanical properties, with substantially high Young's moduli, tensile strengths and elongation at break.

Nevertheless, PIL (NTf_2/PF_6)–20IL membrane is considerably stiffer and strong than that of PIL (NTf_2)–20IL because displays higher Young's modulus and tensile strength and lower elongation at break. The introduction of the bulky $[PF_6]^-$ counter-anion could reduce the flexibility of the PIL polymeric chains and therefore contribute to this difference.

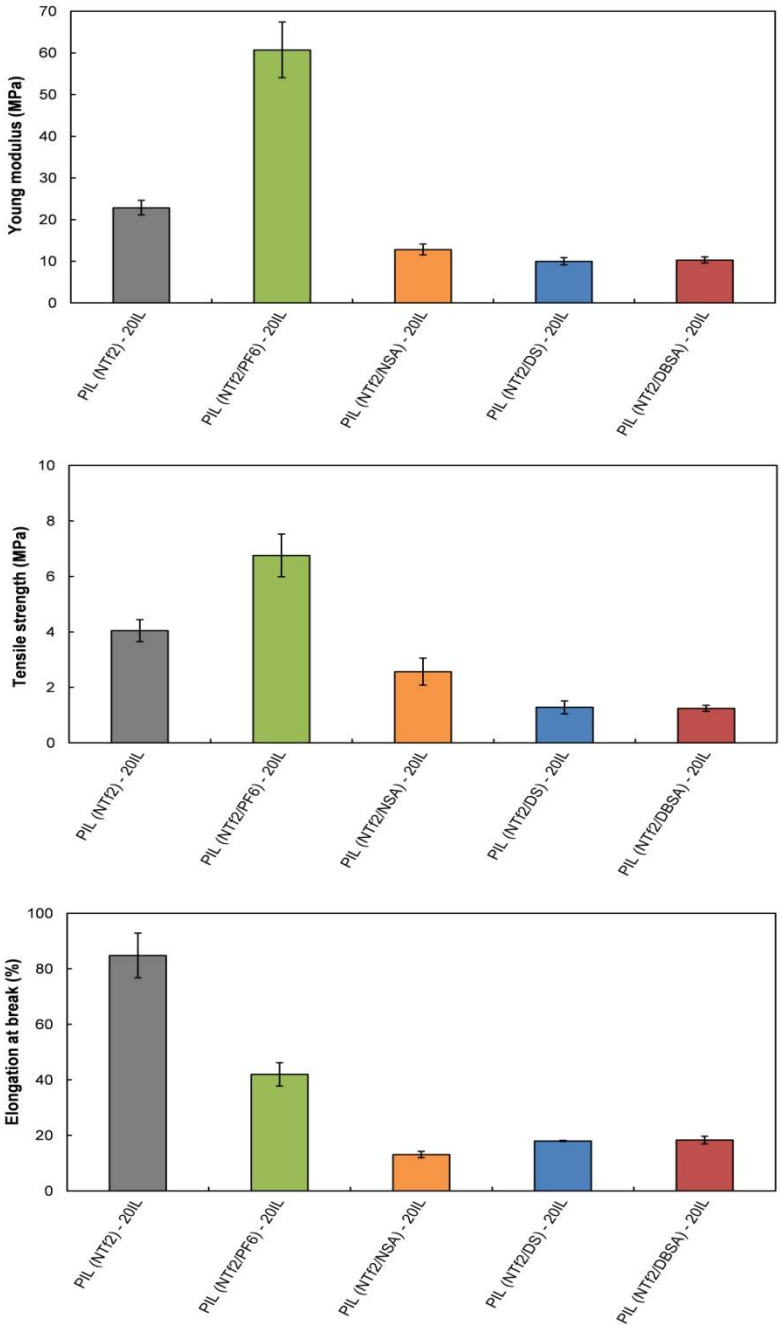


Figure 5| The Young's modulus (top), tensile strength (middle) and elongation at break (bottom) of the prepared composite membranes. Error bars represent standard deviations based on five experimental replicas.

5. Conclusions

Four new PIL random copolymers having pyrrolidinium cation pendant units were synthesized by straightforward salt metathesis reactions directly into the water soluble poly(diallyldimethylammonium) chloride using mixtures of different salts. In order to evaluate the CO_2 separation performance of the synthesized copolymers, free standing composite membranes with 20 wt% of free IL were successfully prepared by the solvent casting method and their permeability, diffusivity and solubility towards CO_2, CH_4, and N_2 were determined. In addition, tensile mechanical properties of the prepared composite membrane, including the Young modulus, tensile strength and elongation at breakage, were also evaluated and discussed.

Results show that the gas permeation properties of the composite membranes can be designed by using pyrrolidinium random copolymers with different counter-anion mixtures as polymer matrices. Depending on the structure of the second counter-anion, the polymer chains interact and pack differently and consequently rigid or further opened polymer networks can be obtained.

Also, the permeability of all gases through composite membranes is mostly related to their gas diffusivities. The prepared composite membranes containing the pyrrolidinium random copolymers have CO_2 permeabilities between 2.74 and 44.2 Barrer, whereas they exhibit permselectivities ranging from 10.8 to 29.3 for CO_2/CH_4 and from 21.4 to 31.0 for CO_2/N_2. Therefore, CO_2 separation performance as a function of permeability can be tuned by using pyrrolidinium random copolymers with different counter-anion mixtures. These results open new possibilities for designing promising pyrrolidinium-based polymeric ionic liquid membranes for CO_2 separation.

Taking into account that membranes with CO_2 separation performances in the upper right quadrant of the Robeson Plots are more attractive for industrial

applications, the development of pyrrolidinium copolymer membranes that possesses high CO_2 permeability is required. To achieve this goal, higher amounts of free IL or other functional free ILs presenting large CO_2 affinities can be incorporated in the membranes. The performance of these materials may also be improved by introducing other chemically different second counter-anions, for instance, by using anions with functional groups such as amines, nitriles, fluorinates or carboxylates in order to create task-specific polymer materials. Indeed, one great advantage of using ionic liquid chemistry is that their chemical and structural designing possibilities are extremely broad.

In conclusion, considering the good CO_2/CH_4 and CO_2/N_2 permselectivities obtained and the simplicity of the polymer synthesis and the membranes procedure, the development of improved CO_2 selective pyrrolidinium random copolymers is an interesting strategy to prepare PIL-based CO_2 separation membranes which deserves to be deeply explored.

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Chapter 7

Pyrrolidinium-based polymeric ionic liquids with cyano counter-anions for CO_2 separation

Adapted from: **L.C. Tomé,** M. Isik, C.S.R. Freire, D. Mecerreyes, I.M. Marrucho, Novel pyrrolidinium-based polymeric ionic liquids with cyano counter-anions: high performance membrane materials for post-combustion CO_2 separation, *submitted manuscript,* 2014.

The author was involved in all the experiments presented herein, as well as on the discussion, interpretation and preparation of the manuscript. The polymers characterization was performed in collaboration with M. Isik.

1. Abstract

In this work, novel pyrrolidinium-based polymeric ionic liquids (PILs) containing different cyano-functionalized counter-anions, namely $[N(CN)_2]^-$, $[C(CN)_3]^-$ and $[B(CN)_4]^-$, were synthesized by straightforward anion exchange reactions and characterized by ^{1}H- and ^{13}C-NMR, FTIR, TGA and DSC analyses. The film forming ability of the PILs blended with 20, 40, and 60 wt% of free ionic liquid (IL) containing similar cyano-functionalized anions was evaluated and the CO_2 and N_2 permeation properties through the prepared composite membranes were determined using a time-lag apparatus. The results show that increasing the IL content in the composite membranes not only increased CO_2 permeability but also boosted the CO_2/N_2 permselectivity leading to improved separation performances. The best performance was achieved for the $[C(CN)_3]$-based composite membrane containing 60 wt% of free IL, which overcomes the Robeson 2008 upper bound, with CO_2 permeability of 439.3 Barrer and CO_2/N_2 permselectivity of 64.4. Therefore, the pyrrolidinium-based PIL combined with the $[C(CN)_3]^-$ as counter-anion has an enormous potential for efficient post-combustion CO_2 separation, suggesting the preparation of high performance membranes for industrial applications.

2. Introduction

During the last decade, ILs have been emerging at the cutting edge of modern chemistry as new alternative solvents.[1] Owing to their exceptional combination of properties (negligible vapor pressure,[2] high ion conductivity,[3] high thermal stability,[4] and low flammability[5]), ILs have been used to promote more efficient processes or develop novel functional materials in a plethora of different technological fields, such as electrochemistry,[6] biotechnology,[7] analytical chemistry,[8] catalysis,[9] energy,[10] nanotechnology,[11] among others. In particular, ILs

have attracted much attention as alternative media for CO_2 capture and separation processes,[12-19] not only due to their low volatility, but also to their highly tunable nature which allows for the design of specific ILs with remarkable affinity for CO_2 over other flue gases.[20-24]

As gas solubility studies in ILs continue to highlight the importance of developing "task-specific" materials for CO_2 capture,[25-35] different engineered approaches have been investigated to take advantage of the desirable properties of ILs for gas separation applications, namely the use of supported ionic liquid membranes (SILMs), in which the IL is immobilized into the pores of a solid inert polymeric membrane.[14] Given that membrane technology has competitive advantages compared to bulky-fluid gas separation, including lower capital costs and energy consumption, small scale equipment and environmentally benign operation,[36] a wide range of different IL phases has been used to develop SILM configurations for CO_2 separation from gas streams.[37-46] Even though some SILMs have shown very impressive CO_2/N_2 separation performances, consistently close or above the 2008 Robeson plot upper bound,[47] their industrial application is limited due to their inadequate long-term stability since they are susceptible to failure if the pressure differential across the membrane is high enough to push out the IL phase from the pores of the membrane support.[14] In order to circumvent this limitation and considering that polymerizable groups can be easily introduced in ILs, polymerized IL-based membranes have been explored as an attractive alternative to SILMs for CO_2 separation.[48]

Polymeric ionic liquids are a new class of functional materials that combine the chemistry of ILs with the macromolecular architecture of polymers,[49-52] providing the opportunity to create a new platform for the design of ionic liquid-based materials for CO_2 separation membranes with significantly improved mechanical stability. In 2006, Noble's group presented neat PIL membranes for CO_2 separation with CO_2/CH_4 and CO_2/N_2 permeability selectivities on par or

greater than those observed for SILMs.[53-56] However, and as expected, there is the substantial drop in both gas permeability and diffusivity through the solid polymer matrix. This fact encouraged Noble's group to re-examine the role of ILs in CO_2 separation membranes, this time by incorporating them in PILs.[57] Bara *et al.* prepared solid stable PIL–IL composite membranes by UV polymerization of imidazolium-IL monomers with 20 wt% of different non-polymerizable ILs (also called "free ILs") and demonstrated that the presence of free IL enables an increase in the CO_2 permeability of PIL-based membranes with little, if no, sacrifice of their CO_2 permselectivities.[58, 59] It is important to point out here that ILs within PILs are different from traditional plasticizers in conventional polymers due, not only to their extremely low volatility at ambient conditions, but also to their ability to strongly interact with the charged backbone of the PIL, through electrostatic interactions. This means that the large degree of electrostatic forces hold the IL within the PIL matrix and prevents phase separation.[57] Moreover, Li *et al*. demonstrated that the incorporation of free IL (ranging from 15 to 60 wt%) into an imidazolium-PIL caused an increase in the free volume of the membranes, while displaying stability under a transmembrane pressure differential of 10 bar.[60] The same group evaluated the performance of PIL–IL composites based on alkyl functionalized vinylimidazolium-PILs having dicyanamide as counter-anion and different free ILs.[61] In this case, the incorporation of the free ILs not only significantly increased the CO_2 permeability but also enhanced the CO_2/N_2 permselectivity.[61]

Although the published data for PIL–IL composite membranes show promising CO_2 permselectivities and large gas permeability improvements, until now the CO_2 separation performance of those membranes has not yet surpassed the 2008 upper bounds on the Robeson plots for CO_2 separations.[47] The lack of diversity in what concerns the different chemical structures of cations and anions is another key issue, since the majority of the efforts to use PIL–IL membranes for

CO_2 separation used imidazolium moieties as pendant groups of the polycation backbone and the bistrifluoromethylsulfonyl)imide ($[NTf_2]^-$) as counter-anion.[57-60, 62-65]

Recently, we studied the gas permeation behavior of PIL–IL composites membranes based on pyrrolidinium ionic liquid materials combining the $[NTf_2]^-$ and demonstrated that their permselectivity/permeability properties are of the same order of magnitude as those of imidazolium-based PILs also containing $[NTf_2]^-$ as counter-anion.[66] In order to increase the flexibility in tailoring their permselectivity/permeability properties, we also explored the use of pyrrolidinium-based PILs with mixtures of counter-anions.[67] The results obtained in the prepared PIL–IL membranes showed that their CO_2 separation performance as a function of permeability can be tuned by using PILs with different counter-anion mixtures, which opened new possibilities to design membrane materials based on pyrrolidinium-PILs for CO_2 separation.[67] It is worth noting that in contrast to the synthetic route of the commonly used imidazolium-PILs, which involves a number of organic syntheses and purification steps at the monomer level, as well as the need of controlled polymerization conditions, the pyrrolidinium-based PILs were particularly simple to prepare since a commercially available polymer was used as the starting material and PILs were prepared through salt metathesis reactions.

Bearing in mind all these aspects, and considering that recent studies have shown that ILs with cyano-functionalized anions present both high CO_2 permeabilities and CO_2/N_2 permselectivities among the different ILs tested so far through SILMs,[43-45] we explore in this work the use of pyrrolidinium-PILs with cyano anions to prepare high performance PIL–IL membrane materials for post-combustion flue gas treatment (CO_2/N_2 separation). This is, to the best of our knowledge, the first report where PILs having a pyrrolidinium polycation backbone combined with different cyano-functionalized counter-anions, namely

dicyanamide ($[N(CN)_2]^-$), tricyanomethane ($[C(CN)_3]^-$) and tetracyanoborate ($[B(CN)_4]^-$), were synthesized by straightforward and efficient anion exchange reactions and characterized. In order to prepare homogenous PIL–IL membranes, the film forming ability of the prepared polymers blended with different amounts of free ILs containing similar cyano-functionalized anions was evaluated. The gas permeation properties, as well as the CO_2/N_2 separation of the formed membranes were also presented.

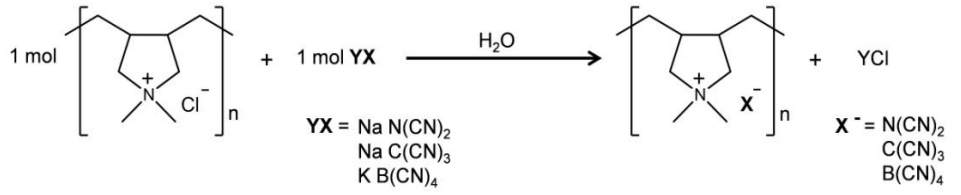
3. Experimental Section

3.1. Materials

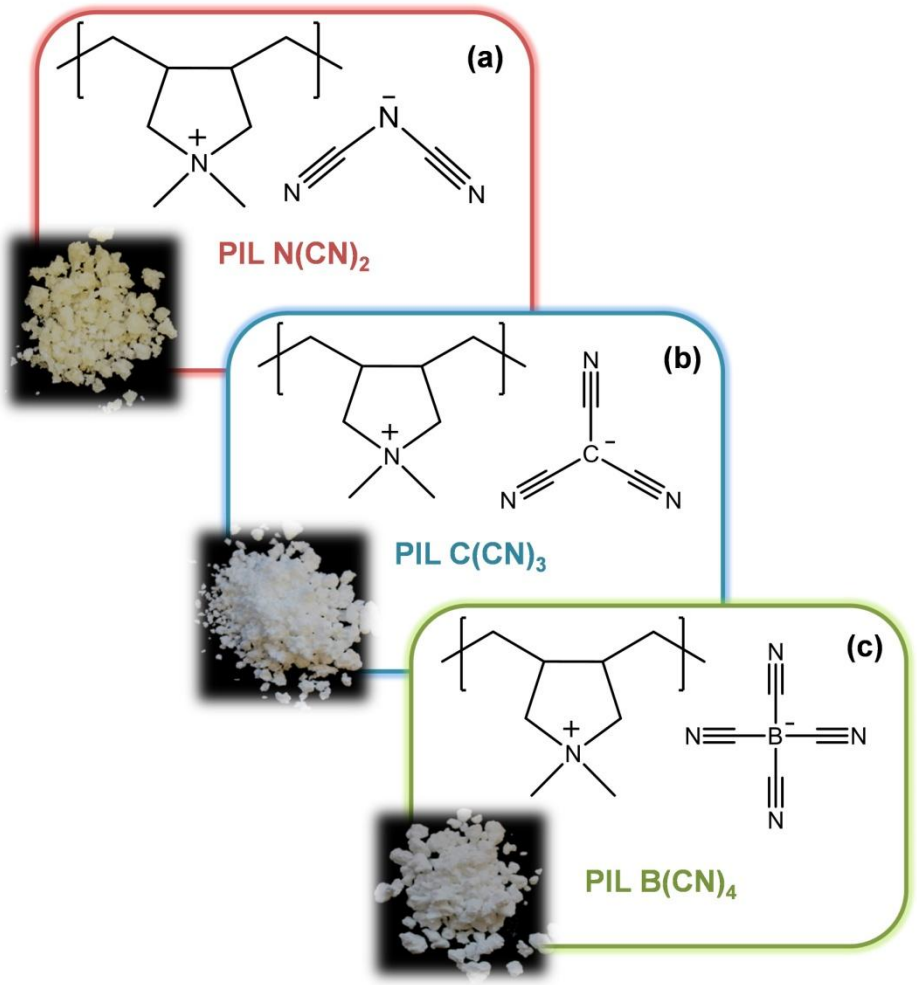
Poly(diallyldimethylammonium) chloride solution (average M_w 400 000–500 000, 20 wt% in water) was supplied by Sigma-Aldrich. IoLiTec GmbH provided the sodium dicyanamide ($NaN(CN)_2$) (> 97 wt% pure), sodium tricyanomethanide ($NaC(CN)_3$) (98 wt% pure), 1-ethyl-3-methylimidazolium dicyanamide ($[C_2mim][N(CN)_2]$) (> 98 wt% pure), 1-ethyl-3-methylimidazolium tricyanomethanide ($[C_2mim][C(CN)_3]$) (> 98 wt% pure). The 1-ethyl-3-methylimidazolium tetracyanoborate ($[C_2mim][B(CN)_4]$) (> 98 wt% pure), was purchased from Merck KGaA Germany. Potassium tetracyanoborate ($KB(CN)_4$), was synthesized as reported elsewhere.[68] In order to reduce the water and other volatile substances content, the ionic liquids were dried under vacuum (10^{-3} kPa) and subject to vigorous stirring at a moderated temperature (≈ 318 K) for at least 2 days immediately prior to use. No further purification of the ILs was carried out, but their purities were further confirmed by ^{1}H- and ^{13}C-NMR analysis and were found to be in accordance with the levels given by the suppliers. All the other solvents were of analytical grade and used as received. CO_2 and N_2, were supplied by Air Liquide and were of at least 99.99% purity.

3.2. Synthesis of pyrrolidinium-based polymers

Polymeric ionic liquids (PILs) containing pyrrolidinium pendant units and cyano-functionalized counter-anions were synthesized by anion exchange reactions from the commercially available polyelectrolyte precursor, poly(diallyldimethylammonium) chloride. In a typical procedure to prepare the poly([pyr_{11}][$N(CN)_2$]) (PIL $N(CN)_2$), a solution of $NaN(CN)_2$ (3.47 g, 38.97 mmol) in 20 mL of distilled water, and a solution of poly(diallyldimethylammonium) chloride (6 g, 37.11 mmol of monomeric units) in 150 mL of distilled water were mixed in a round bottom flask by stirring for 30 min at room temperature. Then, the water was removed by rotary evaporation at 318 K, and afterwards 250 mL of ethanol were added in order to precipitate the NaCl, which is a byproduct of the anion exchange reaction. The precipitate was filtered, and the filtrate was kept at 268 K overnight to complete the precipitation of NaCl, which was then filtered off (this work up was repeated until no more NaCl precipitate was observed). Evaporation of ethanol yielded the PIL containing $[N(CN)_2]^-$ anion as a slightly yellow powder (yield. 80%). As it is shown in Scheme 1, the same anion exchange procedure was successfully used with the other two salts, $NaC(CN)_3$ and $KB(CN)_4$, to prepare the corresponding poly([pyr_{11}][$C(CN)_3$]) (PIL $C(CN)_3$) and poly([pyr_{11}][$B(CN)_4$]) (PIL $B(CN)_4$), respectively. In both cases, the formed polymers became hydrophobic and precipitated in the aqueous media. The obtained white solids (PIL $C(CN)_3$ and PIL $B(CN)_4$) were washed with excess amount of water, filtered and dried in a vacuum oven at 318 K until constant weights were attained (yields > 90%).



Scheme 1| Anion exchange reaction proposed for the synthesis of polymeric ionic liquids containing pyrrolidinium pendant groups and cyano-functionalized anions.



Scheme 2| Chemical structures of the prepared polymeric ionic liquids (PILs): (a) poly([pyr_{11}][$N(CN)_2$]), (b) poly([pyr_{11}][$C(CN)_3$]) and (c) poly([pyr_{11}][$B(CN)_4$]).

3.3. Polymer characterization

The polymeric ionic liquids synthesized in this work were characterized by ^{1}H- and ^{13}C-NMR, Attenuated Total Reflection-Fourier Transform Infrared spectroscopy (ATR-FTIR), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

^{1}H- and ^{13}C-NMR were recorded with a Bruker AC-500 spectrometer. Poly([pyr$_{11}$][N(CN)$_2$] was dissolved in deuterium oxide (D_2O) and both the poly([pyr$_{11}$][C(CN)$_3$]) and poly([pyr$_{11}$][B(CN)$_4$]) were dissolved in dimethyl sulfoxide-d_6 (DMSO-d_6).

FTIR-ATR spectra of the polymers were acquired using a Bruker ALPHA spectrometer. All spectra were collected using 32 scans with a resolution of 2 cm^{-1} from 350 to 4000 cm^{-1}.

The thermal stabilities and decomposition temperatures of the prepared polymers were measured using a thermal gravimetric analyser (TGA Q500, TA Instrument). The samples were placed inside platinum pans and heated up to 1073 K, at a constant rate of 10 K min^{-1}, under a nitrogen atmosphere. The onset (T_{onset}) and the decomposition (T_{dec}) temperatures were determined, as the temperatures at which the baseline slope changes during the heating, and at which 50% of weight loss was observed, respectively.

DSC experiments were performed on a TA Instrument Q2000. Samples (*ca.* 5 to 10 mg) were crimped in non-recyclable aluminium hermetic pans and analyzed under nitrogen atmosphere by heating and cooling cycles at a rate of 10 K min^{-1}. First, the samples were heated to 423 K and kept isothermally for 5 min to erase the thermal history of the samples. Then, they were cooled down to 203 K and kept isothermal for 5 min. Second run heating cycles were conducted and analyzed. The glass transition (T_g) temperatures were determined as the temperature at the midpoint of the glass transition region.

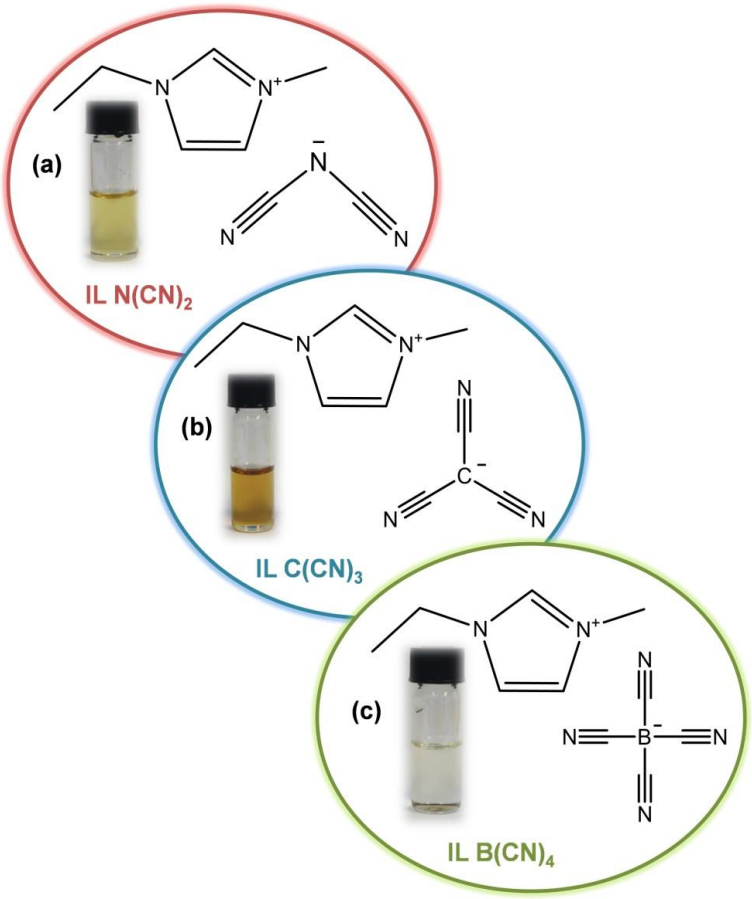
3.4. Membrane preparation

Composite membranes based on the new synthesized PILs (Scheme 2) with different amounts of free IL, containing similar cyano-functionalized anions (Scheme 3), were prepared by solvent casting method. Initially, solutions of each

polymer in appropriate solvents were prepared and the corresponding ionic liquids were added in order to obtain solutions containing different wt% of free IL to the polymer matrix. The solutions were magnetically stirred for 8 hours before being poured into Petri dishes and left for slow evaporation of the solvents. The experimental conditions of the casting process used to prepare the different PIL–IL composite materials are presented in Table 1. Finally, all the composites were dried in a vacuum oven at 318 K until a constant weight was attained.

3.5. Gas permeation measurements

Ideal (i.e., single gas) CO_2 and N_2 permeabilities and diffusivities through the prepared membranes were measured using a time-lag apparatus, described in detail elsewhere.[66] In this work, all the composite membranes were degassed under vacuum inside the permeation cell during 12 hours before testing in order to remove entrained gases and traces of water. The single gas permeation measurements using CO_2 and N_2 were conducted at 293 K with a trans-membrane driving force of 100 kPa upstream against initial vacuum downstream (< 0.1 kPa). At least three separate experiments of each gas on a single membrane sample were carried out. Between each run, the permeation cell and lines were evacuated on both upstream and downstream sides until the pressure was below 0.1 kPa. The thicknesses of the composite membranes tested (120–150 μm) were measured before and after testing using a digital micrometer (Mitutoyo, model MDE-25PJ, Japan). Average thickness was calculated from six measurements taken at different locations of each membrane sample. At the end of the gas experiments, no residual ionic liquid was found inside the permeation cell and, similarly, the membranes mass remained constant.



Scheme 3| Chemical structures of the ionic liquids used to prepare the composite membranes: (a) $[C_2mim][N(CN)_2]$, (b) $[C_2mim][C(CN)_3]$ and (c) $[C_2mim][B(CN)_4]$.

It is usually accepted that gas transport trough a dense polymeric membrane occurs according to the solution-diffusion mass transfer mechanism, whereby the permeability coefficient or permeability (*P*), a measure of the membrane's ability to permeate gas, is the product of diffusivity (*D*) and solubility (*S*) as shown in Equation (1).[69]

$$P = S \times D \quad (1)$$

Permeability (*P*) is defined as the steady-state gas flux (*J*) through a membrane under a transmembrane pressure drop (Δ*p*) and normalized to the unit thickness of the membrane as follows:[70]

$$P = J\frac{\ell}{\Delta p} \tag{2}$$

The flux was determined experimentally using Equation 3, where V^p is the permeate volume, Δp_d is the variation of downstream pressure, *A* is the effective membrane surface area, *t* is the experimental time, *R* is the Ideal Gas Law constant and *T* is the absolute temperature.

$$J = \frac{V^p \Delta p_d}{AtRT} \tag{3}$$

Diffusivity (*D*) was obtained according to Equation 4. The time-lag parameter (θ), which can be obtained before achieving steady-state flux, was deduced by extrapolating the slope of the linear portion of the p_d vs. *t* curve back to the time axis, where the intercept is equal to θ.[71]

$$D = \frac{\ell^2}{6\theta} \tag{4}$$

After knowing both *P* and *D*, it was also possible to calculate *S* using the relationship shown in Equation (1).

The ideal permeability selectivity (or permselectivity), $\alpha_{i/j}$, was obtained by dividing the permeability of the more permeable specie *i* to the permeability of the less permeable specie *j*. As shown in Equation (5), the permselectivity can also be expressed as the product of the diffusivity selectivity and the solubility selectivity.

$$\alpha_{i/j} = \frac{P_i}{P_j} = \left(\frac{D_i}{D_j}\right) \times \left(\frac{S_i}{S_j}\right) \tag{5}$$

Table 1| Composition and experimental conditions of the casting procedure used to prepare the PIL–IL composite membranes.

Composite membranes	Polymer (PIL)	Ionic liquid (IL)	wt% of IL	Solvent	PIL–IL solutions (*w/v*)%	*T* (K)	Evaporation time (days)
PIL $N(CN)_2$–20 IL $N(CN)_2$			20				
PIL $N(CN)_2$–40 IL $N(CN)_2$	Poly([pyr_{11}][$N(CN)_2$])	[C_2mim][$N(CN)_2$]	40	Ethanol	3	308	4
PIL $N(CN)_2$–60 IL $N(CN)_2$			60				
PIL $C(CN)_3$–20 IL $C(CN)_3$			20				
PIL $C(CN)_3$–40 IL $C(CN)_3$	Poly([pyr_{11}][$C(CN)_3$])	[C_2mim][$C(CN)_3$]	40	Acetonitrile	6	313	2
PIL $C(CN)_3$–60 IL $C(CN)_3$			60				
PIL $B(CN)_4$–20 IL $B(CN)_4$			20				
PIL $B(CN)_4$–20 IL $B(CN)_4$	Poly([pyr_{11}][$B(CN)_4$])	[C_2mim][$B(CN)_4$]	40	Acetonitrile	6	313	2
PIL $B(CN)_4$–20 IL $B(CN)_4$			60				

.

4. Results and Discussion

4.1. Synthesis and characterization of pyrrolidinium-based polymers

Two main synthetic routes have been used to prepare pyrrolidinium-based PILs for several applications.[72-82] While the first one involve the synthesis of diallyldimethylammonium ionic liquid monomers with the desired anions followed by polymerization to obtain pyrrolidinium-based PILs with different functionalities,[72-74] the second route is achieved through the anion exchange of the water soluble poly(diallyldimethylammonium chloride) with the appropriated salt.[75-82] The second route is undoubtedly less complex since it has the advantage of obtaining several pyrrolidinium-based PILs directly from the same initial precursor via a simple aqueous purification step.[77] Consequently, in the present work, we used the second synthetic strategy to prepare novel pyrrolidinium-based PILs containing cyano-functionalized counter-anions. As it is represented in Scheme 1, the simple anion exchange procedure was carried out directly into the commercially available poly(diallyldimethylammonium) chloride using different salts, namely $NaN(CN)_2$, $NaC(CN)_3$ and $KB(CN)_4$. As a result, the formed polymers became hydrophobic and precipitated in the aqueous media, with the exception of the less hydrophobic PIL $N(CN)_2$, where an additional ethanol washing step was needed to obtain the pure polymer. The chemical structures of the prepared pyrrolidinium-based PILs are shown in Scheme 2.

The chemical nature of the synthesized polymers was confirmed either by FTIR spectroscopy and NMR analysis. The FTIR spectra of the synthesized PILs are depicted in Figure 1. In the entire spectra, the bands at around 1474 cm^{-1} and the bands between 3030-2860 cm^{-1} are attributed to the $–CH_3$ bending vibration originating from the pendant methyl units of the cationic backbone and $–CH_2$ stretching vibrations, respectively. Moreover, the strong –CN stretching vibrations, at 2127, 2154 and 2220 cm^{-1} for PIL $N(CN)_2$, PIL $C(CN)_3$, and PIL $B(CN)_4$,

respectively, were also observed, indicating the successful incorporation of the corresponding cyano-functionalized counter-anions after the anion exchange reactions.

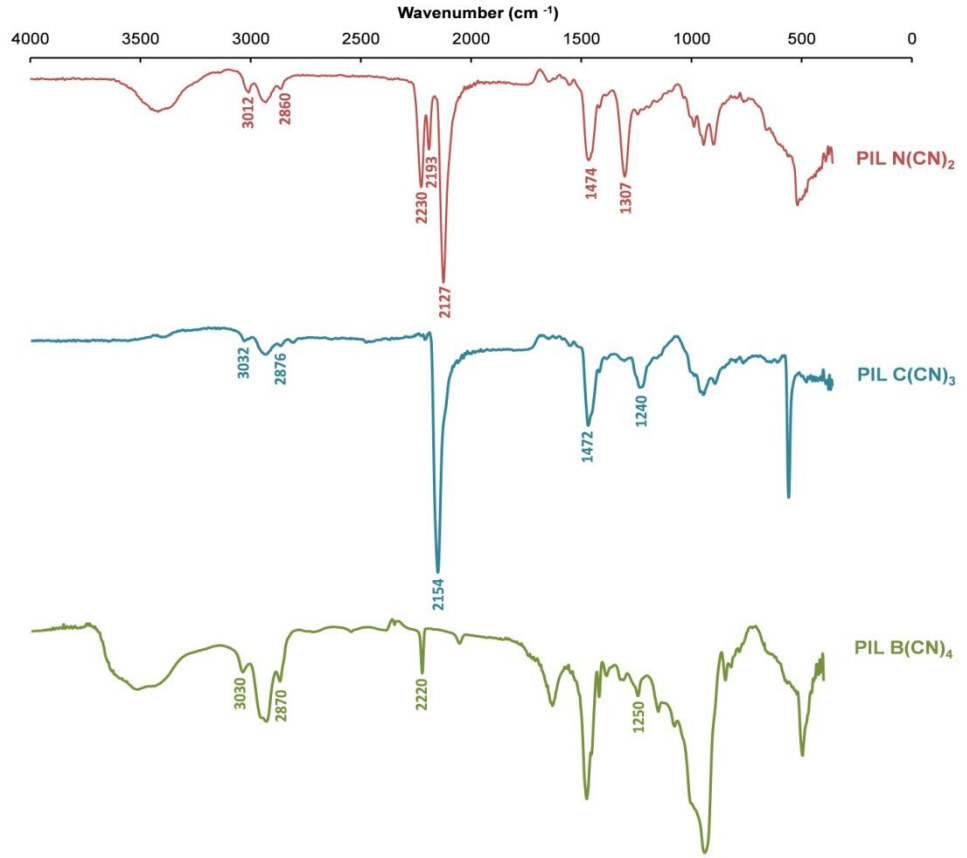


Figure 1| FTIR transmission spectra of the prepared pyrrolidinium-based-PILs.

Similar information can also be obtained from ^{1}H and ^{13}C-NMR analysis. The characteristic chemical shifts arising from the polymer backbone are observed in the ^{1}H-NMR signals of the polymers with different counter-anions as given in Figure 2. The broad signal between 1.00 and 1.75 ppm and the signal at 1.65 ppm are attributed to the methylene (CH_2) and methyne (CH) protons on the backbone, respectively, while the pendant methyl protons (CH_3) are observed at 3.75 ppm. The presence of chemical shifts around 120 ppm in the ^{13}C-NMR spectrum (Figure

3) of all the polymers are attributed to the carbon atoms of each counter-anion, while the signals between 25 and 75 ppm are originate from the cationic backbone.

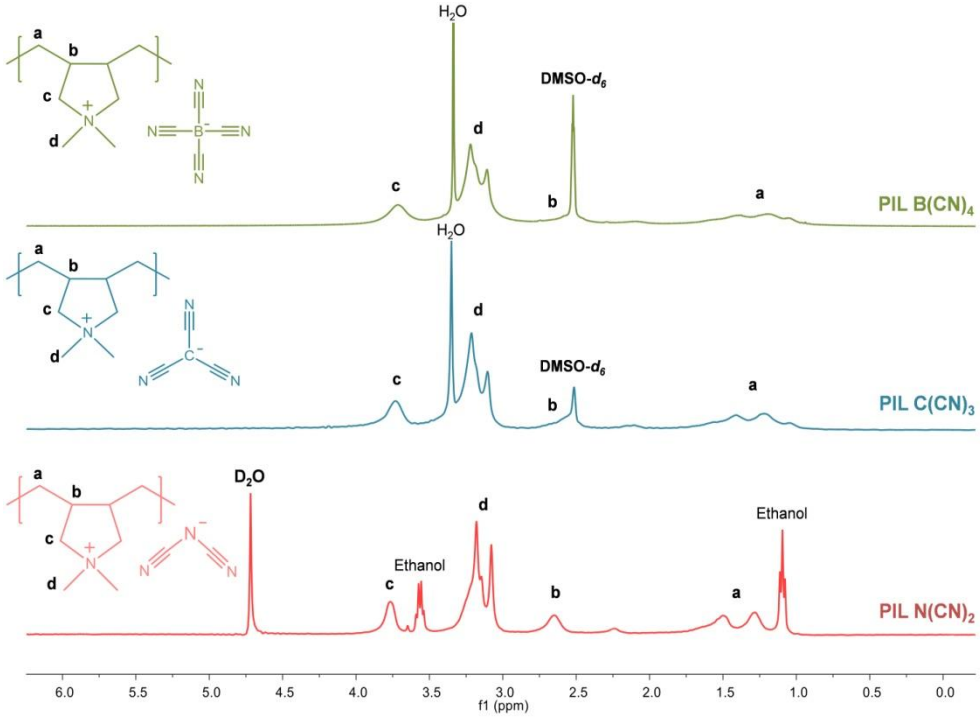


Figure 2| ^{1}H–NMR spectra of the prepared pyrrolidinium-based PILs

Titration tests, which consist in the addition of $AgNO_3$ to solutions of each polymer, were also carried out. For the three synthesized PILs, the titration tests were negative since no precipitation of AgCl occurred, confirming that no chloride counter-anions remained in the PIL structures. Therefore, the silver titration observations combined with the FTIR and NMR analysis corroborated that the anion exchange reactions were quantitative and pure PILs with the desired counter-anions were successfully prepared.

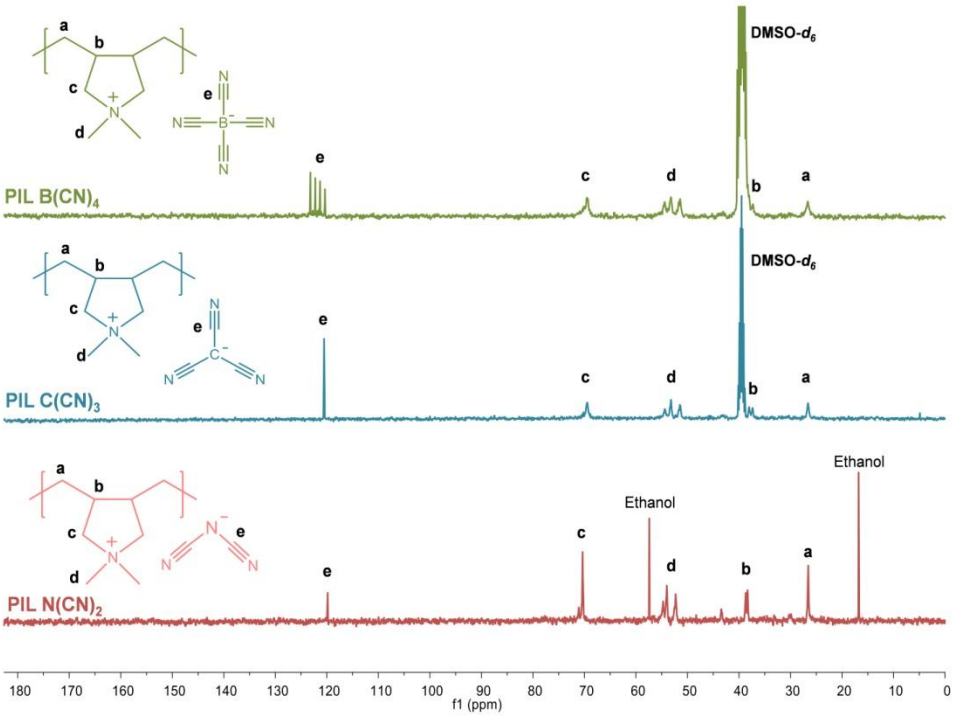


Figure 3| ^{1}H–NMR spectra of the prepared pyrrolidinium-based PILs

The thermal stabilities of the prepared pyrrolidinium-based PILs were studied by TGA analysis in order to determine their decomposition temperatures. As it can be seen in Table 2, the onset temperature (T_{onset}) increased as the number of cyano-functionalized groups increased. However, the same trend was not observed for decomposition temperatures of the polymers, instead the highest T_{dec} was detected for PIL $C(CN)_3$ (788.6 K) and the lowest was obtained for PIL $B(CN)_4$ (727.6 K). The thermal properties of the polymers were further studied by DSC and all the PILs were found to be amorphous having glass transition temperatures (T_g) between 329.4 and 372.8 K. It is worth to remark that both the thermal stability and the glass transition temperatures are higher than those of the original polymer containing chloride as counter-anion (T_{onset} = 548.1 K and T_g = 316.1 K).

Table 2| Thermal properties of the prepared polymeric ionic liquids (PILs) containing different cyano functionalized anions: onset (T_{onset}), decomposition (T_{dec}) and glass transition (T_g) temperatures.

Polymer	T_{onset} (K) [a]	T_{dec} (K) [b]	T_g (K) [c]
PIL $N(CN)_2$	547.0	739.4	329.4
PIL $C(CN)_3$	583.6	788.6	319.9
PIL $B(CN)_4$	592.7	727.6	372.8

[a] T_{onset} defined as the temperature at which the baseline slope changes during the heating.
[b] T_{dec} defined as the temperature at which 50% weight is loss.
[c] T_g defined as the temperature at the middle point of the glass transition region.

4.2. Membrane forming ability

On the contrary to the pyrrolidinium-based PIL with the $[NTf_2]^-$ as counter-anion,[66, 74] the pure PILs synthesized in the present work, which have cyano-functionalized counter-anions, cannot be tested as gas separation membranes in view of the fact that they are unable to be processed into a mechanically stable flat form membrane due to their brittle nature. Since the polymer backbone remains the same, this significantly different behavior of the prepared PILs can be attributed to the rigid nature of their cyano counter-anions when compared to the fluorinated $[NTf_2]^-$ anion, which presents high conformational structural flexibility.

In order to assess the potential of these novel polymers as matrices for gas separation membranes, the film forming ability of the synthesized PILs (Scheme 2) blended with different amounts of free ILs containing similar cyano-functionalized anions (Scheme 3), was evaluated using the solvent casting method. After the initial slow evaporation of the solvents (Table 1), the formed PIL–IL composite membranes were dried in a vacuum oven before being peeled out of the Petri dishes. Pictures of the obtained materials are shown in Figure 4.

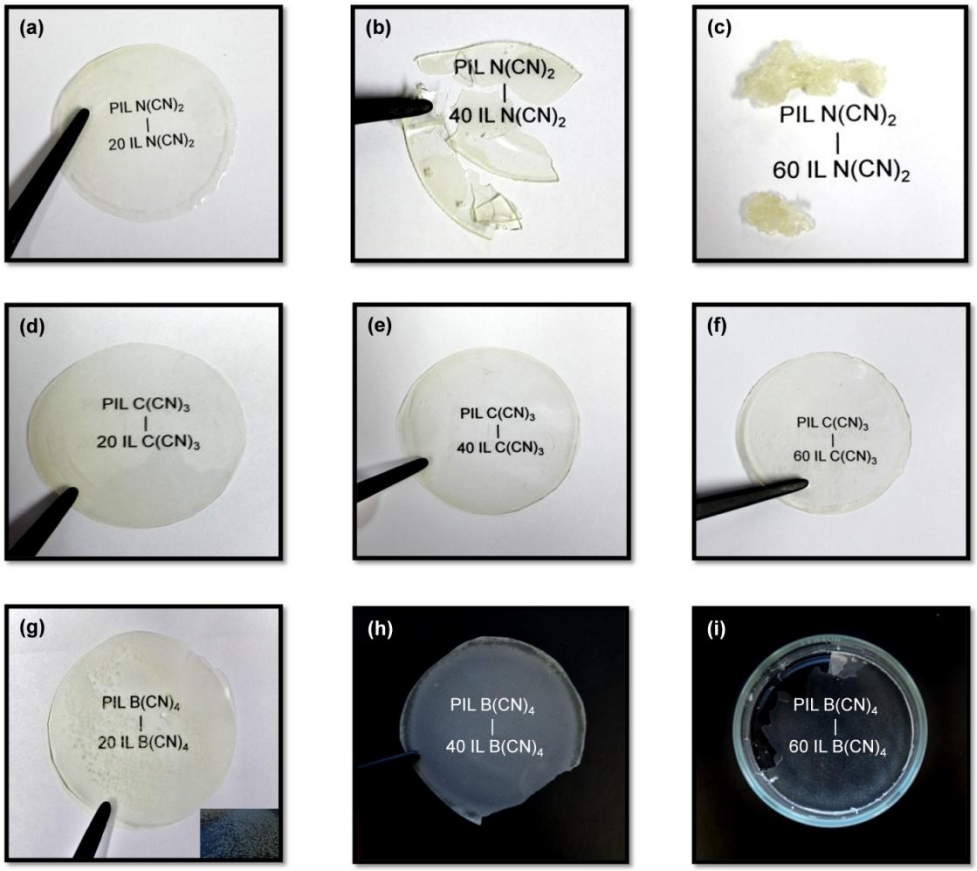


Figure 4| Pictures of the prepared PIL–IL composite materials.

For PIL–IL composites having the $[N(CN)_2]^-$ anion, it was not possible to prepare free standing solid membranes with more than 20 wt% of free IL. Although during the drying process inside the vacuum oven at 318 K, the PIL $N(CN)_2$–IL $N(CN)_2$ composites with 40 and 60 wt% of free IL seem to be solid membranes, they quickly absorb water at ambient conditions due to the hydrophilic nature of the IL ($[C_2mim][N(CN)_2]$) and the composites turn into gel-like materials, as shown in Figures 4 (b) and 4(c), respectively. On the other hand, the composite membranes of the PIL $C(CN)_3$ with 20, 40 and 60 wt% of free IL ($[C_2mim][C(CN)_3]$ were successfully prepared. Actually, all the formed PIL $C(CN)_3$–IL $C(CN)_3$ membranes (Figures 4(d), 4(e) and 4(f)) were homogeneous, flexible with

sufficient mechanical resistance to be handled, and exhibited no evidence of phase separation even after some months of storage under ambient conditions. Regarding the PIL $B(CN)_4$–IL $B(CN)_4$ composite materials, heterogeneous membranes were obtained for all the compositions tested, probably due to the occurrence of segregation between both phases, the PIL $B(CN)_4$ and the IL ($[C_2mim][B(CN)_4]$). As it can be seen in Figures 4(g), 4(h) and 4(i), the prepared composite materials contain a white precipitate, which is clearly visible at naked eye. In conclusion, only four composite membranes were used in the gas permeation studies: one containing the $[N(CN)_2]^-$ anion (PIL $N(CN)_2$–20 IL $N(CN)_2$) and three containing the $[C(CN)_3]^-$ anion (PIL $C(CN)_3$–20 IL $C(CN)_3$, PIL $C(CN)_3$–40 IL $C(CN)_3$, PIL $C(CN)_3$–60 IL $C(CN)_3$).

4.3. Gas permeability, diffusivity and solubility

The measured gas permeability and diffusivity values in the formed PIL – IL membranes are presented in Figure 5 and Figure 6, respectively, while the gas solubility values calculated using Equation (1) are shown in Figure 7.

From Figure 5, it can be seen that the same trend of gas permeability values was obtained for all the PIL–IL membranes tested (P CO_2 >> P N_2), indicating the membranes aptitude to efficiently separate CO_2 from N_2. In fact, the CO_2 permeability is two or more orders of magnitude higher than that of N_2. While the CO_2 permeability values obtained differ from 3.8 to 439.3 Barrer, the N_2 permeabilities range from 0.09 to 6.82 Barrer. A similar behavior was also found for the gas solubility since the N_2 solubility values obtained were significantly lower than those of CO_2, amongst the PIL–IL membranes tested (Figure 7). Although permeability depends on both the gas dissolution into the dense membrane and the gas diffusion through it, the differences in permeability between gases mainly arise from the solubility differences of each gas species.

Thus, the high CO_2 permeability compared to that of N_2 (Figure 5) can be mainly attributed to the high CO_2 solubility relative to N_2 (Figure 7).

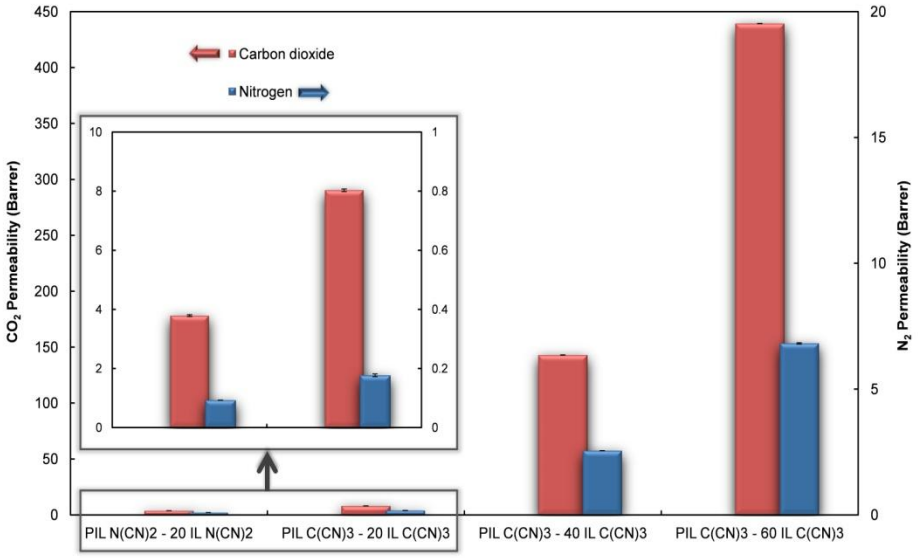


Figure 5| Gas permeabilities (1 Barrer = 10^{-10} cm^3(STP)cm cm^{-2} s^{-1} $cmHg^{-1}$) through the prepared composite membranes. Error bars represent standard deviations based on three experimental replicas.

The PIL–IL composite membranes are blends that combine the gas permeation properties of its constituents, the PIL and the IL. According to Figure 5, the gas permeabilities dramatically increase with the amount of free IL (from 20 to 60 wt%) incorporated into the PIL $C(CN)_3$–IL $C(CN)_3$ membranes, but this increment is not linear. In order words, the gas permeability enhancements between PIL $C(CN)_3$–20 IL $C(CN)_3$ and PIL $C(CN)_3$–40 IL $C(CN)_3$, in which the CO_2 and N_2 permeabilities increased by 1688% and 1322%, are larger than those between PIL $C(CN)_3$–40 IL $C(CN)_3$ and PIL $C(CN)_3$–60 IL $C(CN)_3$, where permeability increments of only 207% and 166% occurred, respectively. Nevertheless, the increments on gas permeabilities through the PIL $C(CN)_3$–IL $C(CN)_3$ membranes can be essentially attributed to the enhancement of polymer chain mobility created by the free ion pairs. As reported in the literature,[60] the incorporation of IL

into PIL not only decrease the glass transition temperature but also increase the free volume of PIL–IL composite, allowing higher polymer chain mobility and consequently enhanced gas permeabilities. This trend when scaling the gas permeability with the IL content into polymer membranes has been recognized by different authors.[66, 81, 83-85]

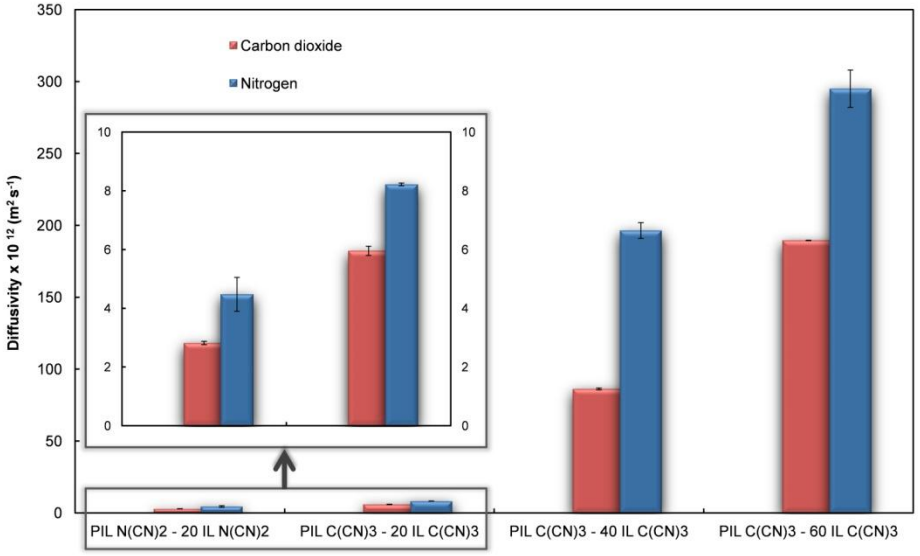


Figure 6| Gas diffusivities through the prepared composite membranes. Error bars represent standard deviations based on three experimental replicas.

Regarding the effect of the cyano-functionalized anions on the gas permeation properties, it can be observed from Figure 7 that changing the PIL and IL chemical structures, through the use of $[N(CN_2)]^-$ instead of $[C(CN)_3]^-$ anion, has no effect on the gas solubilities. Conversely, the PIL $N(CN)_2$–20 IL $N(CN)_2$ presents lower CO_2 and N_2 permeabilities (Figure 5) and diffusivities (Figure 6) than those of the PIL $C(CN)_3$–20 IL $C(CN)_3$, probably owing to the fact that the $[N(CN_2)]^-$ anion has lower molar volume than that of the $[C(CN)_3]^-$ anion and thus, contributes to a more packed membrane structure with less free volume and higher resistance to gas diffusion.

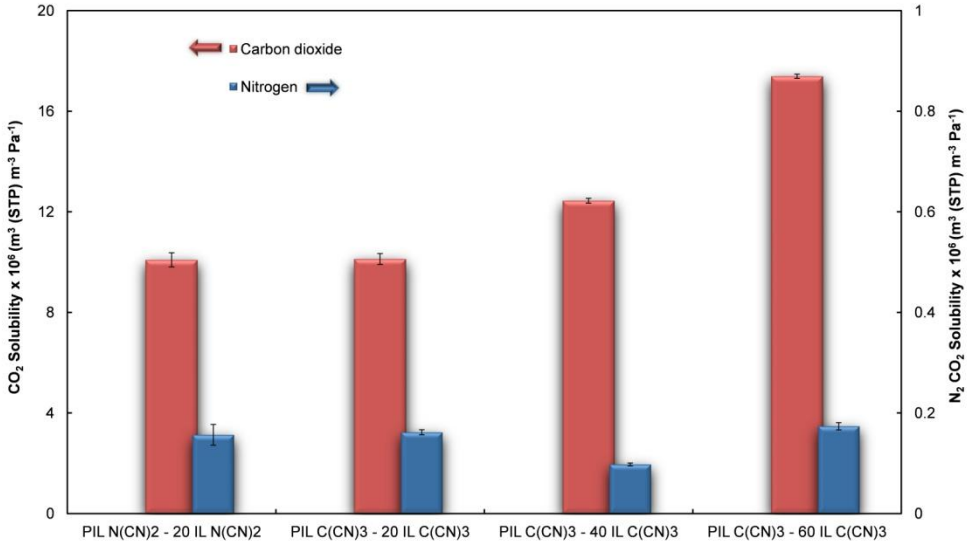


Figure 7| Gas solubilities in the prepared composite membranes, calculated using Equation (1).

In general, we note that the gas permeabilities through all the prepared composites are related to their respective gas diffusivities, with the series from the lowest to the highest permeabilities (Figure 5) being equal to that of their diffusivities (Figure 6). As the increase in gas permeabilities can be mainly attributed to quicker gas diffusion through the membranes and considering that the comparison between Figure 6 and Figure 7 shows higher gas diffusivity increments than those observed for gas solubility, it can be concluded that diffusivity is the primary factor differentiating the gas permeabilities amongst the studied composite membranes.

4.4. CO_2 separation performance

The obtained ideal CO_2 permeability and CO_2/N_2 permselectivity of all the studied PIL–IL composite membranes are summarized in Table 3. Looking at the results obtained for the PIL–IL composites with 20% of free IL having different cyano-functionalized anions, the PIL $N(CN)_2$–20 IL $N(CN)_2$ presents lower CO_2/N_2

permselectivity (40.9) compared to that of PIL $C(CN)_3$–20 IL $C(CN)_3$ (45.4). This behavior is in contrast to what we have previously observed for SILMs, where the pure $[C_2mim][N(CN)_2]$ presented higher CO_2/N_2 permselectivity (67.8) than that of the pure $[C_2mim][C(CN)_3]$-based SILM (57.0).[40, 45] This means that, in the case of the composites blended with only 20 wt% of free IL, the polymer matrix has a great influence on their permselectivity properties that are certainly governed by a molecular-sieving mechanism (diffusivity selectivity) since both the CO_2 and N_2 solubilities are very similar in those composite membranes (Figure 7).

Table 3| Single CO_2 permeability (P)[a] and ideal permselectivities (α) obtained in the prepared PIL–IL composite membranes.[b]

Composite membranes	P CO_2	α CO_2/N_2
PIL $N(CN)_2$–20 IL $N(CN)_2$	3.79 ± 0.03	40.9 ± 0.4
PIL $C(CN)_3$–20 IL $C(CN)_3$	8.03 ± 0.04	45.4 ± 1.4
PIL $C(CN)_3$–40 IL $C(CN)_3$	143.0 ± 0.1	55.9 ± 0.1
PIL $C(CN)_3$–60 IL $C(CN)_3$	439.3 ± 0.1	64.4 ± 0.3

[a] Barrer (1 Barrer = 10^{-10} cm^3(STP)cm cm^{-2} s^{-1} $cmHg^{-1}$)

[b] Errors represent the standard deviations, based on three experiments.

Table 3 shows that the incorporation of higher amount of free IL not only significantly increased the CO_2 permeability but also enhanced the CO_2/N_2 permselectivity by 23% and 42% in PIL $C(CN)_3$–40 IL $C(CN)_3$ and PIL $C(CN)_3$–60 IL $C(CN)_3$, respectively, compared to that of the composite with 20 wt% of IL $C(CN)_3$. Since the diffusivity selectivity (D CO_2/N_2) values of PIL $C(CN)_3$–IL $C(CN)_3$ membranes are in the range of 0.4 to 0.7, the positive effect on their CO_2/N_2 permselectivities by incorporating more free IL is attributed to the higher solubility selectivity increase between the two gases (S CO_2/N_2 from 63 to 127). In other words, the contribution of the solubility-controlled mechanism boosts up as the amount of free IL incorporated increases, and consequently the composite membranes turn into more solubility selective materials, with higher CO_2/N_2

permselectivities. Remarkably, the CO_2/N_2 permselectivity (64.4) herein obtained for the PIL $C(CN)_3$–60 IL $C(CN)_3$ represent the highest value reported so far for PIL–IL membranes.

The comparison of CO_2 separation performance between the results obtained in this work and the previously published data for other PIL-based membranes can be seen in Figure 8, where the CO_2/N_2 permselectivity is plotted against CO_2 permeabilities on the so-called Robeson plot.[47] This type of graph, which is widely used to evaluate the gas separation performance of membrane materials, displays the tradeoff line between permeability and selectivity that has been observed for polymeric membranes. Since the performance of the vast majority of membranes falls below the upper bound 2008, which is based on large amounts of experimental data for CO_2/N_2 separation,[47] data points above this line can be considered as an improvement over the current membrane state of the art.

Figure 8 shows that the CO_2/N_2 separation performances of the membranes combining PILs with cyano-functionalized anions and 20 wt% of free IL are above the upper bound, close to those available in literature for neat PIL membranes and other PIL–IL composites also with 20 wt% of free IL. However, their CO_2/N_2 permselectivities are greater (40.9 – 64.4) than those previously reported (21.4 to 32.0) for PIL–20 IL composites prepared with diverse pyrrolidinium-based PIL matrices.[67] Furthermore, the incorporation of higher contents of free IL into PIL $C(CN)_3$ causes a dramatic shift of the separation performance results along the *x*-axis. As a result the PIL $C(CN)_3$–40 IL $C(CN)_3$ is very close to the upper bound for CO_2/N_2 separation, while the PIL $C(CN)_3$–60 IL $C(CN)_3$ surpasses it, indicating its enormous potential for post-combustion flue gas treatment. With increasing the IL content up to 60 wt%, the PIL $C(CN)_3$–IL $C(CN)_3$ membranes gained more "liquid-like" behavior and their CO_2/N_2 separation performance further deviates from that of the PIL $C(CN)_3$ and approaches the Robeson plot region of the $[C_2mim][C(CN)_3]$-based SILM (Figure 8). Consequently, the PIL–IL membranes prepared herein do

not follow the traditional tradeoff between permselectivity and permeability usually observed for polymeric membranes, where more permeable membranes tends to exhibit less permselectivity and vice versa.

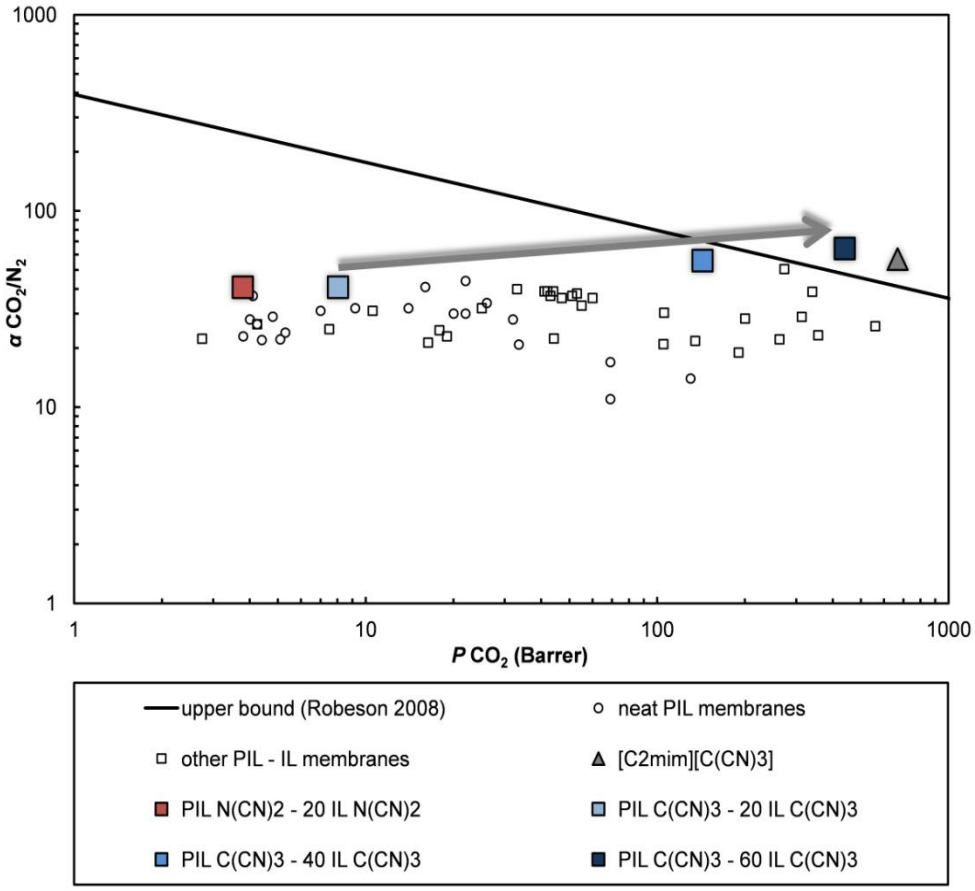


Figure 8| CO_2/N_2 separation performances of the formed composite membranes. Experimental error is within the data points. Data are plotted on a log-log scale and the upper bound is adapted from Robeson.[47] For comparison, literature data reported for (□) other PIL–IL membranes and (○) neat PIL membranes.[54-62, 65-67] The $[C_2mim][C(CN)_3]$-based SILM is also plotted for comparison and its values were taken from Tomé *et al*.[45]

5. Conclusions

Three novel PILs having a pyrrolidinium polycation backbone combined with cyano-functionalized counter-anions were synthesized by salt metathesis reactions directly into the water soluble poly(diallyldimethylammonium) chloride. The NMR and FTIR analysis combined with the silver titration experiments corroborate that the anion exchange reactions were quantitative and pure PILs with high thermal stabilities were successfully prepared. Since the nature of the pure PILs was very brittle and their films easily broke, PIL – IL membranes were prepared with different contents of free IL and the CO_2 and N_2 permeation properties of the formed membranes were determined and discussed.

Results shows that the presence of different cyano-functionalized anions has no effect on the gas solubilities of PIL–20 IL membranes, but depending on the number of cyano groups in the anion, different gas permeabilities and diffusivities can be obtained. Concerning the free IL effect, the incorporation of higher IL contents into the pyrrolidinium-based PIL with the $[C(CN)_3]^-$ counter-anion not only dramatically increased the gas permeabilities and diffusivities through the composite membranes but also enhanced their CO_2/N_2 permselectivities. Overall, the contribution of the solubility-controlled mechanism rises by increasing the IL content and thus the composite membranes turn into solubility selective materials with "liquid-like" CO_2/N_2 separation performance behavior. Remarkably, the performance of the formed PIL $C(CN)_3$–40 IL $C(CN)_3$ nearly achieved the Robeson 2008 upper bound for CO_2/N_2 separation, while the PIL $C(CN)_3$–60 IL $C(CN)_3$ surpassed it.

Although further research on long-term chemical and mechanical stability, as well as the effect of different experimental conditions (temperature, pressure and humidity) is needed to entirely understand its potential, this work highlights for the first time a PIL–IL membrane that outperforms the Robeson 2008 upper

bound for CO_2/N_2 separation, which opens the possibility to re-think the potential of PIL matrices in terms of efficiency to prepare high performance membrane materials for practical post-combustion CO_2 separation processes.

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Chapter 8

Polymeric ionic liquid membranes containing IL–Ag^+ for ethylene/ethane separation

Adapted from: **L.C. Tomé,** D. Mecerreyes, C.S.R. Freire, L.P.N. Rebelo, I.M. Marrucho, Polymeric ionic liquid membranes containing IL–Ag^+ for ethylene/ethane separation via olefin-facilitated transport, *J. Mater. Chem. A*, 2014, **2**, 5631-5639. (cover of the issue).

The author was involved in all the experimental work presented herein, as well as on the discussion and preparation of the manuscript.

1. Abstract

This work focuses on the separation of light olefins from their corresponding paraffins using membranes due to their lower energy consumption and operating costs in comparison to the traditionally used methods which are highly energy intensive. Although polymeric ionic liquids (PILs) have attracted much attention as interesting materials to prepare improved gas separation membranes, their exploitation for light olefin/paraffin separation has never been attempted before. In this work, we propose the use of PILs as alternative polymer matrices for olefin/paraffin separation. A new series of facilitated transport membranes of poly([pyr_{11}][NTf_2]) incorporating different amounts of the ionic liquid (IL) ([C_4mpyr][NTf_2]) and the silver salt ($AgNTf_2$) were prepared by a solvent casting process and their ethane (C_2H_6) and ethylene (C_2H_4) permeation properties were measured. The results show that the preparation of PIL/IL composite membranes increases the permeability of both C_2H_4 and C_2H_6, overcoming the hindered gas diffusion in the pure PIL. Nevertheless, the presence of the IL in the composite membrane promotes reduced C_2H_4/C_2H_6 permselectivity. The addition of the silver salt greatly boosts the solubility of the olefin in the membranes. Furthermore, increasing the silver ion concentration in the PIL/40IL system leads to enhanced overall C_2H_4/C_2H_6 permselectivity surpassing the upper bound for polymeric membranes, indicating that PILs have interesting potential as polymer matrices for olefin-facilitated transport membranes.

2. Introduction

The separation of olefin and paraffin gases, produced in several stages of the petrochemical industry, such as steam cracking, catalytic cracking, or paraffin dehydrogenation, is of vital importance since olefins are essential building blocks for many products and chemicals.[1] Cryogenic distillation is being used to perform

the separation of olefins such as ethylene and propylene from their corresponding paraffin-rich streams. However, the distillation process requires high amounts of energy and equipment costs due to the very small vapor pressure difference between the olefin and paraffin species.[1-3] Given that the separation of lower saturated and unsaturated hydrocarbons having the same number of carbons is one of the most difficult, costly and energy intensive processes in the petrochemical and chemical industries, research targeted at developing new energy-saving and cost-effective processes for olefin/paraffin separation is in high demand.

In this context, the use of membrane technology for olefin/paraffin separation has been proposed as an attractive alternative to current cryogenic distillation,[3-6] mainly due to its inherent advantages, including small scale of the equipment, relative environmental safety, low energy consumption and operating costs.[7] However, the results obtained[8-12] show that the application of conventional polymeric membranes for olefin/paraffin separation is not very attractive for industrial proposes because olefins and paraffins have similar molecular sizes and solubilities, resulting in poor separation performances. In view of that, many researchers have directed their attention to the use of facilitated transport membranes[13, 14] by the incorporation of a carrier compound that can selectively and reversibly react with the desired gas enhancing its transport across the membrane. It is well known that olefins can form reversible complexes with transition-metal cations, such as silver (Ag^+), *via* π-bond complex formation mechanism where the olefin works as electron donor and the metal cation as electron acceptor.[14-17] Even though these bonds are stronger enough to achieve high selectivities, they can easily be reversed by pressure and temperature swing.[18]

Several works have been published on the separation of olefin/paraffin using different types of facilitated transport membranes, in the solid state, having Ag^+ as

an olefin carrier.[19-27] Supported liquid membranes containing aqueous silver salt solutions have also been widely studied since they present higher gas diffusions compared to solid membranes leading to higher gas permeabilities.[28-31] Unfortunately, the stability of these membranes is affected by liquid depletion through evaporation.[14] To circumvent this problem, the most interesting strategy proposed is the use of ionic liquids owing to their intrinsic properties such as negligible volatility,[32] high thermal stability,[33] and low flammability.[34] Particular attention has been paid to supported ionic liquid membranes (SILMs) containing silver salts[35-39] since ILs offer high olefin retention capacity and stability to the solubilized metal cations acting as medium for facilitated transport.[40-43] Nevertheless, SILMs configurations still have the mechanical stability issue unsolved and their application in industry is limited to low trans-membrane pressure differentials due to the risk of expelling the IL from the pores of the support.[44] Different approaches have been explored to overcome the pressure stability problems inherent to SILMs. For instance, facilitated transport ion-gel membranes have been developed using imidazolium-based ILs and silver salts.[45] The use of polymer/IL composite membranes has also proposed as potential alternative. Fallanza *et al.*[46] have successfully prepared and tested facilitated transport membranes based on poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and 1-butyl-3-methylimidazolium tetrafluoroborate ($[C_4mim][BF_4]$) containing silver tetrafluoroborate ($AgBF_4$) for separating propylene/propane mixtures. Nevertheless, the best way to approach ILs for gas separation using membranes is to polymerize IL monomers and prepare solid polymer membranes.[47]

Polymeric ionic liquids have attracted increasing interest over the past few years since they combine some of the unique properties of ILs with the improved mechanical stability and macromolecular architecture of polymers.[48, 49] Pioneering studies anticipated their use as advanced polymer electrolytes,[50-52] but this new

class of polyelectrolytes has also been finding an increasing number of applications in other technological fields.[48, 49] In particular, the separation of CO_2 from N_2 or CH_4 through specifically designed PIL/IL composite membranes, with high CO_2 separation performances, has been widely investigated.[53-60] Although such PIL/IL composites seem to be a promising strategy for obtaining improved gas separation membranes, its exploitation for olefin/paraffin separation has never been attempted.

In order to evaluate the viability of using PILs as polymeric matrices for light olefin/paraffin separation, novel facilitated transport membranes of poly([pyr_{11}][NTf_2]), incorporating different compositions of ionic liquid and silver salt mixture (IL–Ag^+) were prepared and gas permeation experiments using ethane and ethylene were performed. The PIL used herein is particularly simple to prepare, since a commercially available polymer is used as a starting material and the PIL is obtained solely by straightforward salt metathesis reaction. The $[NTf_2]^-$ was chosen as the PIL counter-anion due to its high thermal stability. The IL, [C_4mpyr][NTf_2], was selected not only due to its similarity to the PIL monomeric unit but also because similar ILs with smaller chains in the cation are solid at room temperature. Galán Sánchez *et al*.[41] showed that higher ethylene absorption capacity can be achieved combining ILs having the $[NTf_2]^-$ anion and a salt with the same anion as the source of the silver ions. Accordingly, $AgNTf_2$ was used as olefin carrier in the present study. The chemical structures of the materials used are shown in Figure 1. This is, to the best of our knowledge, the first report exploring the use of polymeric ionic liquids as matrices to prepare facilitated transport membranes for ethylene/ethane separation.

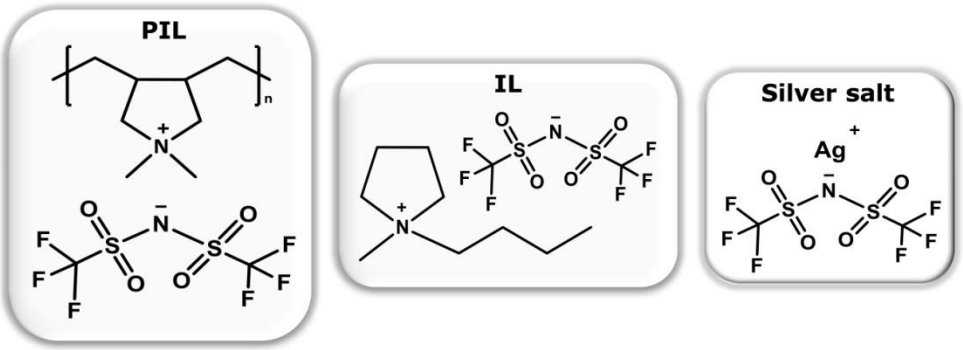

Figure 1| Chemical structures of the materials used to prepare the membranes: poly([pyr_{11}][NTf_2]) (PIL), [C_4mpyr][NTf_2] (IL) and $AgNTf_2$ (silver salt).

3. Experimental Section

3.1. Materials

Poly(diallyldimethylammonium) chloride solution (average Mw 400 000–500 000, 20 wt% in H_2O) and silver bis(trifluoromethylsulfonyl)imide ($AgNTf_2$, 97%) were purchased from Sigma-Aldrich. 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([C_4mpyr][NTf_2], 99%) and lithium bis(trifluoromethylsulfonyl)imide ($LiNTf_2$, 99%) were supplied by IoLiTec GmbH. All the other solvents were of analytical grade and used as received. C_2H_6 and C_2H_4 were provided by Air Liquide with a minimum purity of 99.9%.

3.2. Membrane preparation

Poly([pyr_{11}][NTf_2]) (PIL) containing pyrrolidinium pendants units and $[NTf_2]^-$ as the counter-anion was synthesized by an anion exchange reaction from the commercially available poly(diallyldimethylammonium) chloride, according to a procedure described elsewhere.[61] Subsequently, membranes based on the synthesized PIL were prepared by the solvent casting method following an established procedure:[59] the PIL was first dissolved in acetone (12% (w/v)) and

then the IL ([C_4mpyr][NTf_2]), with or without the silver salt ($AgNTf_2$) dissolved, was added. Mixtures of IL containing different concentrations of $AgNTf_2$ were previously prepared by magnetic stirring until the complete dissolution of the silver salt. The solutions in acetone were magnetically stirred for 8 hours, before being poured into Petri dishes and left to evaporate slowly at room temperature under dark conditions for 48 hours. Free standing composite membranes were prepared (Table 1), with the exception of those containing IL compositions higher than 60 wt%, where liquid mixtures were obtained. Porous hydrophobic poly(vinylidene fluoride) (PVDF) membranes, with a pore size of 0.22 μm, average thickness of 125 μm, acquired from Millipore Corporation (USA), were used to support the pure IL ([C_4mpyr][NTf_2]) and the liquid mixture of PIL/80IL. The supported ionic liquid membrane (SILM) configurations were prepared according to our previously reported procedure.[60]

3.3. Gas permeation measurements

Gas permeabilities and diffusivities through the prepared membranes were measured using a time-lag apparatus. Details on the construction and operation of this experimental setup are entirely described elsewhere.[59] Briefly, this system consists of two chambers (feed and permeate) separated by a flat-type permeation cell. Each prepared membrane was positioned on the top of a highly porous sintered disk for providing mechanical stability and installed into the flat-type permeation cell (Figure 2), where it was degassed under vacuum during 24 hours before testing. The single gas permeation experiments using C_2H_6 and C_2H_4 were performed at 293 K with an upstream pressure of 100 kPa (feed) and vacuum (<0.1 kPa) as the initial downstream pressure (permeate). At least three separate experiments of each gas on a single membrane sample were carried out, and the experimental error was found to be less than 3%. Between each run, the permeation cell and lines were evacuated on both upstream and downstream

sides until the pressure was below 0.1 kPa. At the end of the gas experiments, it was checked if the IL remained entrapped inside the porous support or the polymer matrix and that no carrier degradation had occurred. The thicknesses of the prepared solid composite membranes (95–110 μm) were measured before and after testing using a digital micrometer (Mitutoyo, model MDE-25PJ, Japan). Average thickness was calculated from six measurements taken at different locations of each membrane sample. On the other hand, the thickness of the prepared SILMs was assumed to be equivalent to the membrane filter thickness.

The gas transport through dense membranes occurs according to a solution-diffusion mass transfer mechanism, whereby the permeability (*P*), which is a measure of the membrane's ability to permeate gas, is the product of solubility (*S*) and diffusivity (*D*) as it is shown in Equation (1).[62]

$$P = S \times D \tag{1}$$

Permeability (*P*) is defined as the steady-state gas flux (*J*) through a membrane under a transmembrane pressure drop (Δp) and normalized to the unit thickness of the membrane as follows:[63]

$$P = J \frac{\ell}{\Delta p} \tag{2}$$

The flux was determined experimentally using Equation 3, where V^p is the permeate volume, Δp_d is the variation of downstream pressure, *A* is the effective membrane surface area, *t* is the experimental time, *R* is the Ideal Gas Law constant and *T* is the absolute temperature.

$$J = \frac{V^p \Delta p_d}{AtRT} \tag{3}$$

Diffusivity (*D*) was obtained according to Equation 4. The time-lag parameter (θ), which can be obtained before achieving steady-state flux, was deduced by

extrapolating the slope of the linear portion of the p_d vs. t curve back to the time axis, where the intercept is equal to θ.[64]

$$D = \frac{\ell^2}{6\theta} \tag{4}$$

After knowing both P and D, it was also possible to calculate S using the relationship shown in Equation (1).

The ideal permeability selectivity (or permselectivity), $\alpha_{i/j}$, was obtained by dividing the permeability of the more permeable specie i to the permeability of the less permeable specie j. As shown in Equation (5), the permselectivity can also be expressed as the product of the diffusivity selectivity and the solubility selectivity.

$$\alpha_{i/j} = \frac{P_i}{P_j} = \left(\frac{D_i}{D_j}\right) \times \left(\frac{S_i}{S_j}\right) \tag{5}$$

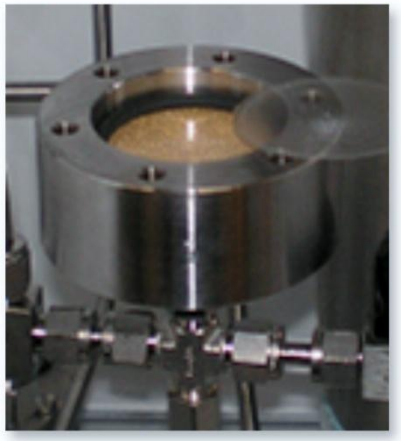

Figure 2| Stainless steel flat-type permeation cell used in this work.

4. Results and Discussion

The composition description of the prepared membranes is detailed in Table 1. Initially, different amounts of free IL were incorporated into the PIL in order to understand the gas permeation behavior throughout the whole material range, from PIL to IL, encompassing PIL/IL composites. It is important to point out that ILs (and thus IL–Ag^+ mixtures) within PIL matrices are different from traditional plasticizers in conventional polymers due, not only to their negligible vapor pressure, but also to their ability to strongly interact with the charged backbone of the PIL through electrostatic interactions.

Single C_2H_6 and C_2H_4 permeation experiments through the prepared membranes were carried out using a time-lag apparatus, which allows for the simultaneous determination of permeability and diffusivity. The influence of the different IL amounts incorporated into the PIL matrix, as well as the concentration effect of silver ions on the C_2H_6 and C_2H_4 permeabilities, diffusivities, solubilities and the C_2H_4/C_2H_6 permselectivity were studied.

Table 1| Identification and composition of the membranes prepared.

Membrane	poly([pyr_{11}][NTf_2]) (wt%)	[C_4mpyr][NTf_2] (wt%)	$AgNTf_2$ (M)	PVDF as support
Pure PIL	100	-	-	-
PIL/20IL	80	20	-	-
PIL/40IL	60	40	-	-
PIL/40IL–Ag^+ 0.5M	60	40	0.5	-
PIL/40IL–Ag^+ 0.75M	60	40	0.75	-
PIL/40IL–Ag^+ 1M	60	40	1.0	-
PIL/40IL–Ag^+ 1.25M	60	40	1.25	-
PIL/60IL	40	60	-	-
PIL/80IL	20	80	-	✓
Pure IL	-	100	-	✓

4.1. Effect of ionic liquid content

In order to understand the effect of IL content on the gas permeation properties of the composite membranes without silver salt, single gas permeation experiments using C_2H_4 and C_2H_6 were first performed in membranes with compositions ranging from the pure PIL (free standing polymeric membrane) to pure IL (supported ionic liquid membrane), covering different PIL/IL composites. The measured gas permeability and diffusivity values are shown in Figures 3(a) and (b), respectively, while the gas solubility values calculated using Equation (1) are presented in Figure 3(c).

The obtained permeability value of the pure IL ([C_4mpyr][NTf_2]) towards C_2H_4 (102.1 Barrer) is of the same magnitude order of those reported in literature for other imidazolium-, phosphonium- and ammonium-based SILMs, also determined by the time-lag method.[44, 65, 66] For the prepared membranes, from the pure PIL to the pure IL, the C_2H_4 permeability values vary from 0.29 to 102.1 Barrer, respectively, while the C_2H_6 permeabilities differ from 0.10 to 55.5 Barrer (Figure 3(a)). For all the studied membranes, C_2H_4 permeability is always greater than that of C_2H_6. The same trend was observed for both gas diffusivity (D C_2H_4 > D C_2H_6) (Figure 3(b)) and solubility (S C_2H_4 > S C_2H_6) (Figure 3(c)). The higher diffusion of the olefin is probably due to the fact that the C_2H_4 not only has smaller molecule size but also minor length of the C=C bond than that of C-C in C_2H_6.[67] Furthermore, it is well known that olefins experience stronger solvation in ILs compared to paraffins.[41, 42, 68-70] The solubility trend (S C_2H_4 > S C_2H_6) obtained in this work for the pure PIL and the PIL/IL composite membranes (Figure 3(c)) are in fine agreement with this behavior.

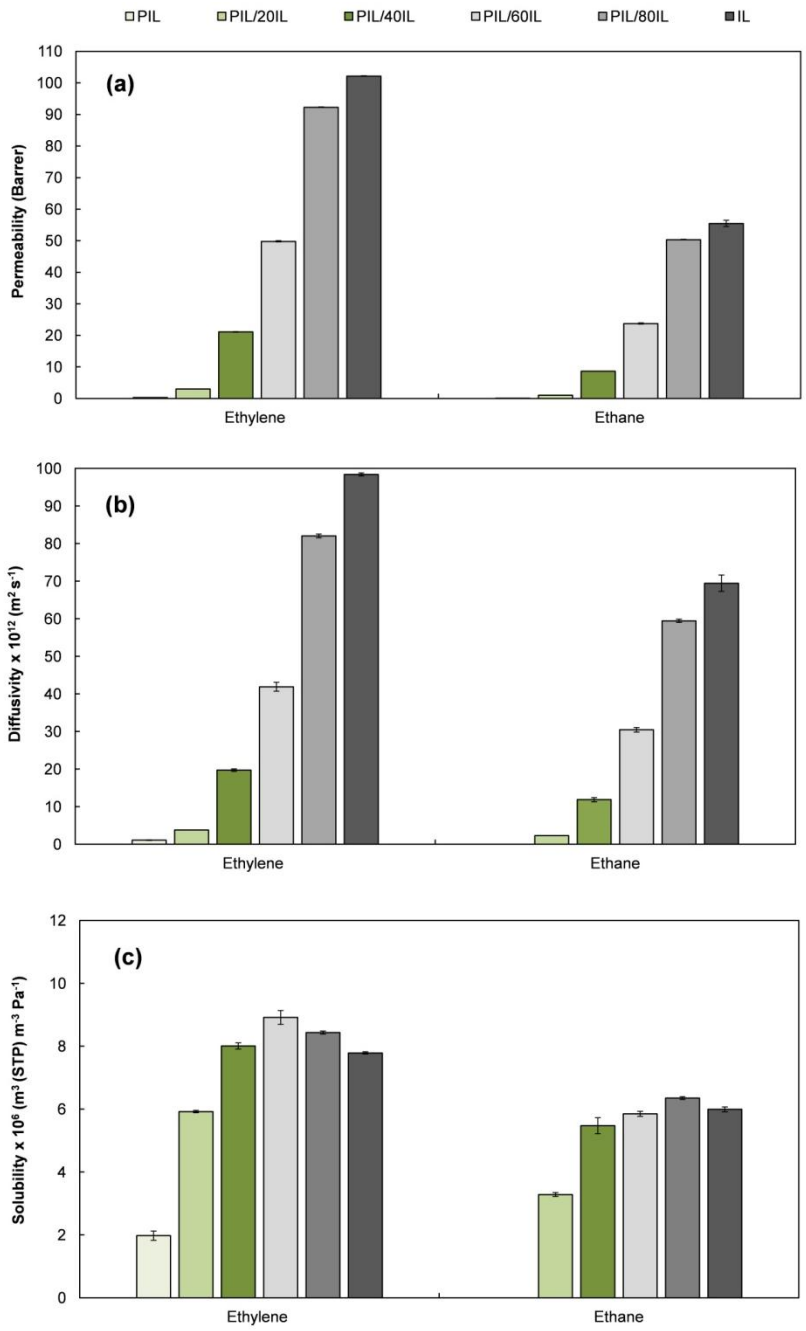

Figure 3| Effect of IL content on the ethane and ethylene (a) permeability, (b) diffusivity and (c) solubility through the prepared pyrrolidinium-based membranes without silver salt. Error bars represent standard deviations based on three experimental replicas. Sensitivity of the apparatus prevented a reliable measurement of C_2H_6 time-lag in the pure PIL membrane and, consequently, the determination of solubility and diffusivity.

The results presented in Figure 3(a) show that the permeability towards the gases studied in PIL/IL composites is much improved compared to that of pure PIL membrane. For instance, the addition of 20 wt% of IL into PIL increases C_2H_4 and C_2H_6 permeabilities by 931% and 900%, respectively while, for the PIL/40IL composite, permeability enhancements of 7176% and 8550% occurred. This increment of permeabilities can be clearly attributed to quicker gas diffusion through the composite membranes due to the presence of free IL. Actually, the C_2H_4 and C_2H_6 diffusivities in the PIL/IL composites increase with the amount of free IL incorporated (Figure 3(b)), probably due to the enhancement of polymer chain mobility created by the free ion pairs. On top of that, upon a comparison of diffusivity (Figure 3(b)) and solubility (Figure 3(c)) data, it is clear that the increment of gas diffusivity was the dominating factor for the gas permeability enhancement obtained in the prepared PIL/IL composite membranes.

4.2. Effect of silver concentration

In order to investigate the influence of the silver salt concentration on the C_2H_4 and C_2H_6 permeation properties through membranes having a polymeric ionic liquid as matrix, PIL/40IL–Ag^+ membranes with four different concentrations of dissolved $AgNTf_2$ were prepared (Table 1, Figure 4). The C_2H_4 and C_2H_6 permeability values measured in the prepared PIL/40IL–Ag^+ membranes are plotted in Figure 5(a), while diffusivity and solubility values are shown in Figures 5(b) and (c), respectively.

As discussed above, increasing the amount of free IL incorporated into the PIL, the membranes gained more “liquid-like” gas permeability and diffusivity behavior, but solid and stable free standing composite membranes of poly([pyr_{11}][NTf_2]) and [C_4mpyr][NTf_2] can be only obtained up to 60 wt% of IL. Due to its intrinsic high permeability, the PIL/60IL composite seemed to be the best choice to incorporate the silver salt. However, during the membranes

preparation we observed that ionic liquid/silver salt phase separation occur within the PIL/IL-Ag membrane when 60 wt% of IL was used. For that reason, the membrane of PIL with 40 wt% of IL was chosen to incorporate the silver salt. All the prepared PIL/40IL–Ag^+ membranes were homogeneous and exhibited no evidence of phase separation.

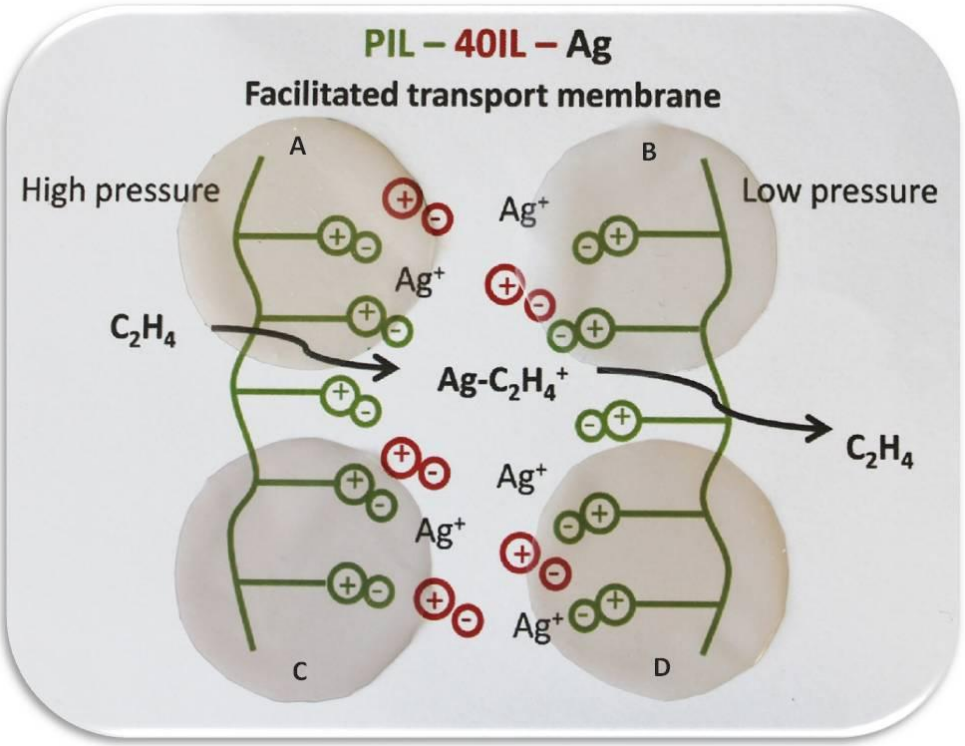

Figure 4| Examples of prepared pyrrolidinium-based membranes containing IL–Ag^+ mixtures: (A) PIL/40IL–Ag^+ 0.5M, (B) PIL/40IL–Ag^+ 0.75M, (C) PIL/40IL–Ag^+ 1M and (D) PIL/40IL–Ag^+ 1.25M.

Figure 5(a) shows that membranes containing IL–Ag^+ possess C_2H_4 and C_2H_6 permeabilities that were substantially different than those of PIL/40IL. It is possible to observe that both C_2H_4 and C_2H_6 permeabilities in PIL/40IL–Ag^+ membranes gradually decreases with the silver concentration, following a linear trend. Data presented in Figure 5(b) suggest that the decrease in permeabilities can be mainly attributed to lower gas diffusion through the composites containing

silver salt when compared to PIL/40IL membrane. Probably the silver salt strong interaction with the IL contributes for a more packed structure with less free volume, and consequently to a higher resistance to gas diffusion. It can also be observed in Figure 5(b) that C_2H_4 diffuses much slower than C_2H_6 in PIL/40IL–Ag^+ membranes. Although C_2H_4 has smaller molecule size, only the C_2H_4 coordinate to the silver ions, while the C_2H_6 can move much freely. This is in good agreement with previous results published by Fallanza *et al.,*[38] who observed a decrease of propylene diffusivity in [C_4mim][BF_4]-based SILM with an increase of silver tetrafluoroborate concentration.

In what concerns solubility, Figure 5(c) shows that the C_2H_6 solubility remains almost the same after the incorporation of silver salt, while the C_2H_4 solubility is greatly enhanced when compared to the PIL/40IL composite membrane. For example, the addition of Ag^+ 0.5 M increases the C_2H_4 solubility by 571%, whereas for the PIL/40IL–Ag^+ 1.25M, a solubility enhancement of 1275% was observed. Most likely, the C_2H_4 solubility is enhanced by the formation of the olefin-metal complex. As expected, the results obtained confirm that only the C_2H_4 forms a complex with the silver ion carrier providing increased solubility of the olefin in the membrane.

4.3. Ethylene/ethane selectivity

The C_2H_4/C_2H_6 permselectivities of all the studied membranes are summarized in Table 2. The incorporation of 20 wt% of IL into the PIL did not significantly affects the C_2H_4/C_2H_6 permselectivity, conversely a permselectivity decrease of 21% and 40% was observed for PIL/40IL and PIL/60IL, respectively. The composite membranes of PIL/IL are blends that combine the C_2H_4/C_2H_6 separation properties of the PIL and that of the IL. Since the permselectivity of C_2H_4/C_2H_6 for the IL is lower than that for the pure PIL (Table 2), the presence of the IL in the composite membrane promotes reduced C_2H_4/C_2H_6 separation efficiency.

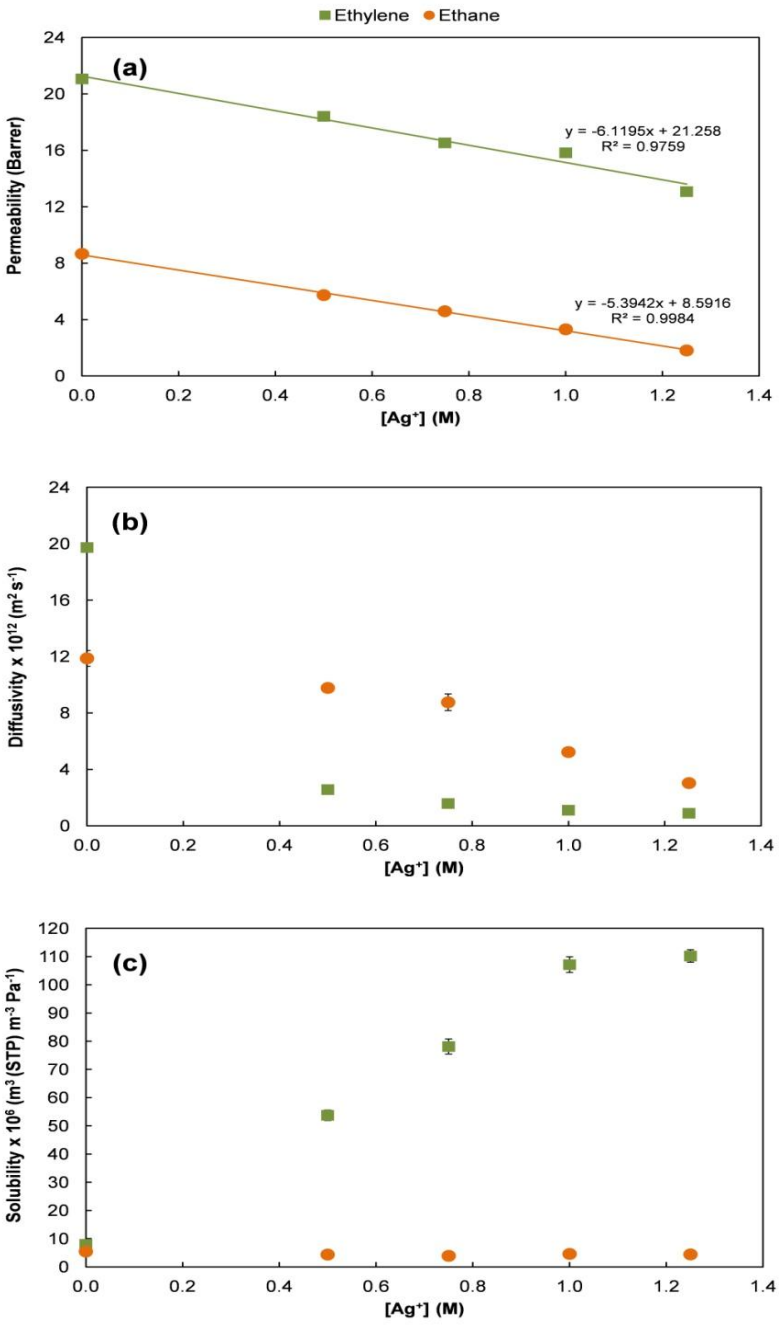

Figure 5| Effect of silver ion concentration on the ethane and ethylene (a) permeability, (b) diffusivity and (c) solubility through the prepared PIL/40IL-Ag^+ membranes. The error is either within the size of the markers or shown by error bars, which represent standard deviations based on three experimental replicas.

Table 2| Single C_2H_4 permeability (P)[a] and ideal permselectivity (α) obtained for all the prepared pyrrolidinium-based membranes.[b]

Membrane	P C_2H_4	α C_2H_4/C_2H_6
Pure PIL	0.29 ± 0.01	2.93 ± 0.08
PIL/20IL	2.99 ± 0.01	2.99 ± 0.04
PIL/40IL	21.1 ± 0.1	2.43 ± 0.02
PIL/40IL–Ag^+ 0.5M	18.4 ± 0.1	3.21 ± 0.02
PIL/40IL–Ag^+ 0.75M	16.5 ± 0.2	3.60 ± 0.17
PIL/40IL–Ag^+ 1M	15.8 ± 0.1	4.79 ± 0.07
PIL/40IL–Ag^+ 1.25M	13.1 ± 0.3	7.24 ± 0.17
PIL/60IL	49.8 ± 0.2	2.10 ± 0.03
PIL/80IL	92.2 ± 0.1	1.83 ± 0.01
Pure IL	102.1 ± 0.1	1.84 ± 0.04

[a] Barrer (1 Barrer = 10^{-10} cm^3(STP)cm cm^{-2} s^{-1} $cmHg^{-1}$)

[b] Errors represent the standard deviations, based on three experiments.

The effect of the concentration of silver ions on the C_2H_4/C_2H_6 permselectivities, diffusivity selectivity and solubility selectivity of the PIL/40IL–Ag^+ membranes is illustrated in Figures 6(a), (b) and (c), respectively. The addition of silver ions in the PIL/40IL system increases the olefin permselectivity (Figure 6(a)). The highest C_2H_4/C_2H_6 permselectivity of 7.24 was attained with the PIL/40IL–Ag^+ 1.25M membrane (Table 2). The improvement of C_2H_4/C_2H_6 permselectivity can be attributed to the large enhancement of C_2H_4/C_2H_6 solubility selectivity (Figure 6(c)) observed in the membranes containing silver ions, since their C_2H_4/C_2H_6 diffusivity selectivities did not considerably change (Figure 6(b)). It can thus be concluded that the C_2H_4/C_2H_6 permselectivity in the PIL/40IL–Ag^+ composite membranes is essentially dominated by solubility selectivity.

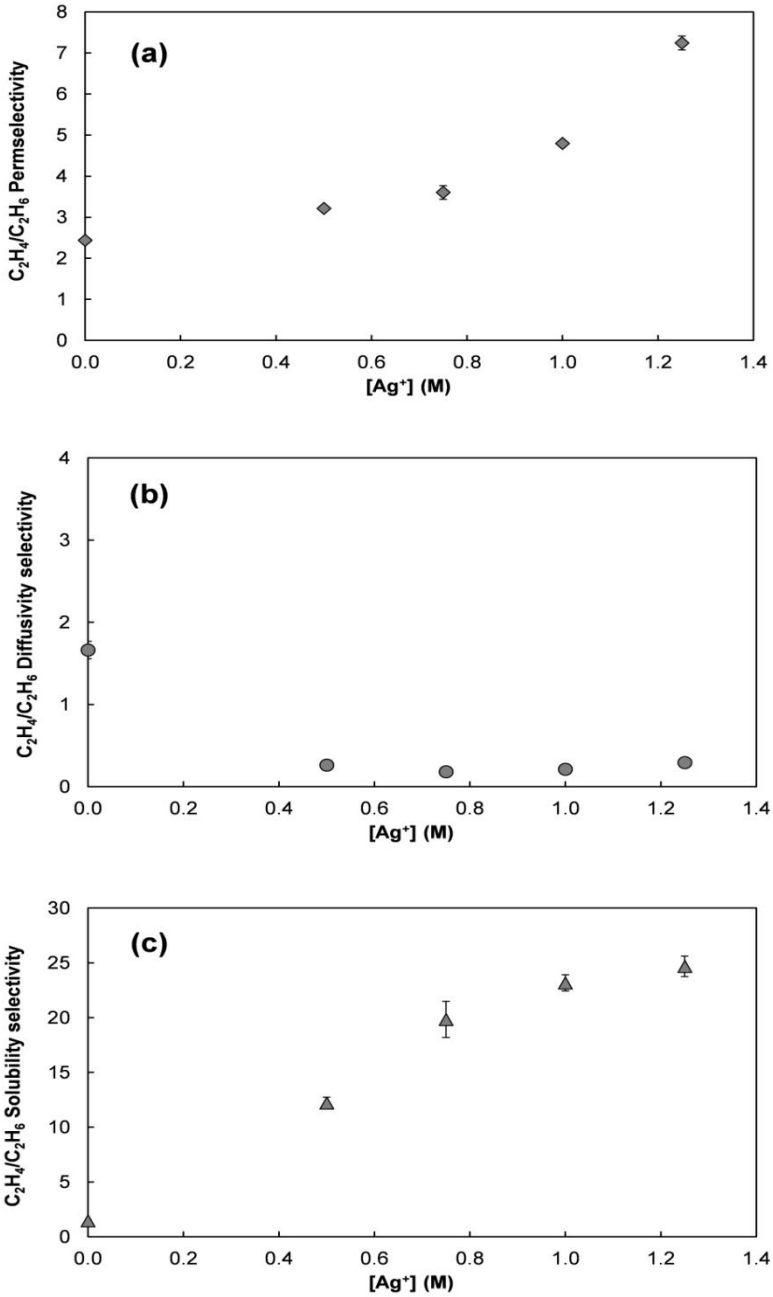

Figure 6| (a) Permselectivity, (b) diffusivity selectivity and (c) solubility selectivity of C_2H_4/C_2H_6 in the prepared PIL/40IL-Ag^+ membranes containing different silver ion concentrations, from 0 to 1.25 M. The error is either within the size of the markers or shown by error bars, which represent standard deviations based on three experimental replicas

4.4. Ethylene separation performance

The measured C_2H_4 permeabilities and the C_2H_4/C_2H_6 permselectivities of all the studied membranes are summarized in Table 2. These results are also plotted in Figure 7, where the permselectivity between C_2H_4 and C_2H_6 is represented *versus* the C_2H_4 permeability. This type of plot, which is commonly used to evaluate the performance of materials given a particular gas separation illustrating the progress in membrane science for gas separation, displays the tradeoff line between permeability and selectivity for gas separation using polymeric membranes. Also referred as "upper bound", this tradeoff relationship shows that the separation factor for a gas pair ($\alpha_{i/j}$) of interest changes inversely to the permeability of the more permeable specie (*i*).[71]

Recently, Koros *et al.*[72] proposed an experimental upper bound for the separation of C_2H_4/C_2H_6 anchored in high-performing 6FDA-based polyimide membranes. The authors also presented a theoretical prediction of the C_2H_4/C_2H_6 upper bound, which was in very good agreement with the determined experimental upper bound.[72] Therefore, we compare in Figure 7 the results obtained in the present work with the experimental polymeric upper bound proposed by Koros.[72] Other sets of relevant data published for polyimide and copolyimide membranes,[9, 11, 72, 73] glassy polymeric membranes,[5, 74] and polymer/silver salt composite membranes [13, 14, 75-77] were also included.

Figure 7 shows that the results obtained for the membranes without silver salt (from pure PIL to pure IL passing through their composites) are all bellow the polymeric ethylene/ethane upper bound performance and over the same plot region of other reported membranes based on polyimides and glassy polymers. It is also clear that the permeability influence of adding IL into PIL is much greater that the addition of PIL into IL. The incorporation of 20 wt% of IL into PIL causes a dramatic shift of the results along the *x*-axis without significantly sacrificing of the

C_2H_4/C_2H_6 permselectivity, whereas when 20 wt% of PIL is added to IL a very small change in C_2H_4 permeability is observed.

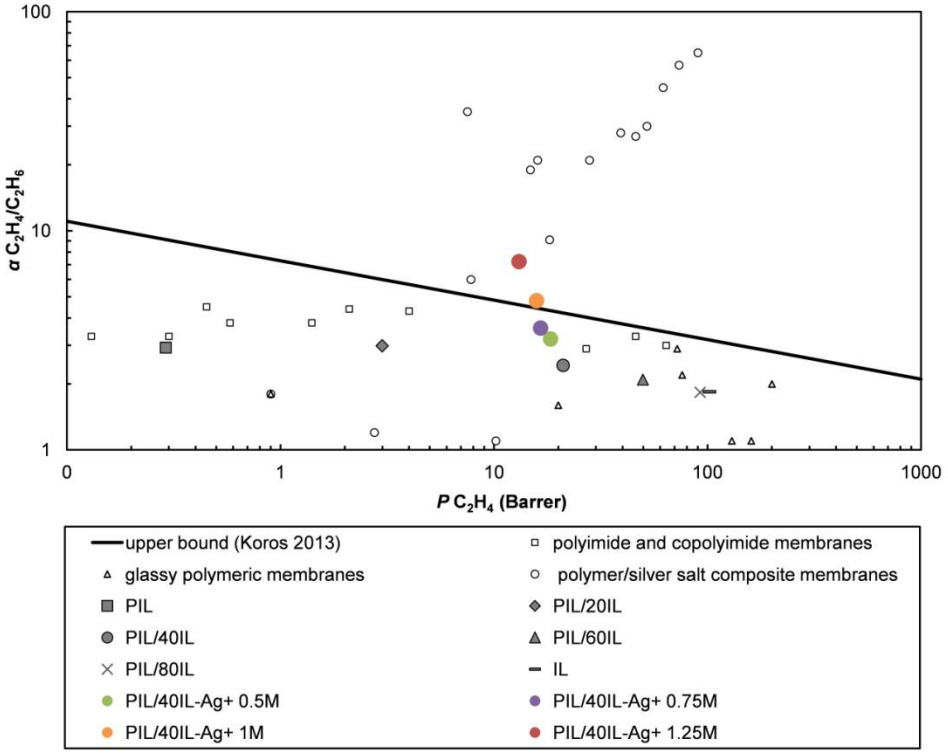

Figure 7| Ethylene separation performance of the studied membranes. Experimental error is within the data points. Data are plotted on a log-log scale and the upper bound is adapted from Koros [72]. Literature data reported for other membranes are also plotted.[5, 9, 11, 13, 14, 72-77]

It can also be seen from Figure 7 that the addition of silver salt into the PIL/40IL has a great impact on the C_2H_4/C_2H_6 separation performance of the composite membranes. Increasing the silver ion concentration in the PIL/40IL membrane leads to a significant shift of the results along the *y*-axis. Besides, the ethylene separation performance of both the PIL/40IL–Ag^+ 1M and PIL/40IL–Ag^+ 1.25M membranes is above the upper bound. This improved performance is certainly due the presence of silver ions, which selectively and reversibly bind to the olefin, increasing the solubility selectivity (Figure 6(c)) and leading to enhanced overall permselectivity surpassing the polymer upper bound (Figure 7).

Even though several reported facilitated transport membranes (illustrated in Figure 7 as polymer/silver salt composite membranes) were able to achieve exceptional permselectivity of C_2H_4 over C_2H_6 with separation performances that are far beyond the polymeric C_2H_4/C_2H_6 upper bound, a direct comparison with the PIL/40IL–Ag^+ membranes prepared in this work cannot be made because of the differences on membrane composition, namely the large silver ion concentration that were added into those reported membranes. In fact, it should be possible to improve the ethylene separation performance of the PIL/IL–Ag^+ prepared herein by using different ionic liquids with higher C_2H_4/C_2H_6 permselectivity or by incorporating superior amounts of silver salt.

5. Conclusions

Polymeric ionic liquid composite membranes based on poly([pyrr$_{11}$][NTf_2]), [C_4mpyr][NTf_2] and silver salt ($AgNTf_2$) were successfully prepared by the solvent casting method. It is important to note that the PIL used in this work was particularly simple to prepare from the commercially available poly(diallyldimethylammonium) chloride through salt metathesis reaction. The single ethane and ethylene permeation properties through the prepared membranes were determined. The influence of the ionic liquid content incorporated, as well as the concentration effect of silver ions on the C_2H_6 and C_2H_4 permeabilities, diffusivities, solubilities and the C_2H_4/C_2H_6 permselectivity of the membranes was studied. In addition, the ethylene separation performance of all the prepared membranes was evaluated and discussed.

The study of the full material range elucidated the role of the ionic liquid on the permeation properties of the composite membranes. Although the incorporation of free IL dramatically increases the C_2H_4 and C_2H_6 permeabilities and diffusivities, its presence in the membranes promotes reduced C_2H_4/C_2H_6 permselectivity.

The addition of IL–Ag^+ decreases the permeability towards both gases the C_2H_4 and C_2H_6, when the silver concentration increases from 0 to 1.25 M. Nevertheless, only the C_2H_4 forms a complex with the silver ion carrier providing increased solubility of the olefin in the membrane, while the C_2H_6 solubility remains almost the same, and consequently the C_2H_4/C_2H_6 permselectivity in the PIL/40IL–Ag^+ facilitated transport membranes are essentially dominated by solubility selectivity.

Regarding the ethylene separation performance, it was found that the membranes without silver salt are bellow the polymeric ethylene/ethane upper bound performance. Conversely, increasing the silver ion concentration in the membranes leads to enhanced overall C_2H_4/C_2H_6 permselectivity and both the PIL/40IL–Ag^+ 1M and PIL/40IL–Ag^+ 1.25M membranes are above the upper bound.

In conclusion, considering the good ethylene separation performances obtained and taking into account that the performance of PIL/IL–Ag^+ membranes may be possible improved by introducing different ILs with higher C_2H_4/C_2H_6 permselectivity or by incorporating superior amounts of silver salt, this work highlighted for the first time that polymeric ionic liquids can be considered as potential alternative polymer matrices to prepare olefin-facilitated transport membranes. Therefore, further research on long-term chemical and mechanical membrane stability is needed and perhaps even the development of an intrinsically stable carrier may be required for making these membranes practical for industrial applications.

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Chapter 9

Concluding Remarks & Outlook

“Some people think design means how it looks.
But of course, if you dig deeper, it’s really how it works.”

Steve Jobs

The research work described in this thesis aimed at designing new efficient gas separation membranes based on ionic liquid (IL) materials. The most important results obtained during this PhD project are highlighted in this chapter. The main achievements and conclusions, as well as some challenges, are described in two sections following the different membrane approaches explored: the development of supported ionic liquid membranes (SILMs); and the design of PIL–IL composite membranes. Finally, the outlook for future research is also presented.

1. Developing supported ionic liquid membranes

Although a broad diversity of ionic liquids, covering the most commonly used cations and anions, has been used to develop SILMs for CO_2 separation,[1] the ecotoxicity of these liquid phases has been overlooked. Aiming at full sustainability of membrane-based CO_2 separation processes, and simultaneously considering that the use of carboxylated anions which have been shown to provide high CO_2 solubilities, SILMs based on environmental-friendly cholinium carboxylate ILs were successfully prepared (Chapter 2).

While the CO_2/CH_4 permselectivity of the cholinium-based SILMs exceeded that of the prototypical ILs,[1-6] the CO_2/N_2 permselectivity is on par or greater. Overall, improved CO_2 permselectivities and high CO_2 solubilities were obtained; however, the permeability of the prepared SILMs toward dry gases is lower compared to that of other families of ILs. The major bottleneck of using cholinium carboxylates is their high viscosities, which lead to long absorption equilibrium times, and low permeabilities. Thus, reducing their viscosity is certainly an important issue. One possible and easy way for increasing the gas permeability through these SILMs is to reduce the IL viscosity by the addition of small amounts of water. It is well reported that the viscosity of ILs drops when they absorb water.[7] Actually, a certain amount of moisture usually exists in real gas streams

and thus it would be economically interesting to use these streams without any further treatment. Therefore, the influence of different amounts of water on both gas permeability and the CO_2 separation performance of cholinium-based SILMs deserves to be further explored.

Given the above mentioned results regarding the low gas permeability through SILMs containing carboxylated anions, and taking advantage of IL mixtures as a mean to further increase the flexibility in tailoring the permeability and permselectivity of these membranes, several IL mixtures were specifically prepared and tested as liquid phases in SILM configurations for CO_2 separation (Chapter 3). Since the anions of ILs have a stronger influence on CO_2 solubility than the cations,[8-10] binary IL mixtures containing a common cation ($[C_2mim]^+$) and anions with different functional groups (carboxylated, fluorinated, sulfate and cyano-functionalized anions) were explored. Imidazolium-based ILs were selected to conduct these studies due to their commercial availability. The results indicated that depending on the anions, SILMs with tailored gas permeabilities, diffusivities and solubilities can be obtained. Remarkably, the SILMs prepared with IL mixtures containing the cyano-functionalized anions exceeded or achieved the upper bound of CO_2/N_2 separation.

Noteworthy, in these studies, rather than just determining the gas permeation properties and evaluating the CO_2 separation performance of the prepared SILMs, a special effort was made to understand how the mixture of ILs with different anions can influence the gas transport behavior. It was found that mixing anions with specific chemical features allows variations in IL viscosity and molar volume that consequently impact the gas permeation properties of SILMs. For instance, higher CO_2 solubility selectivity improvements were obtained by mixing $[NTf_2]^-$ with $[Ac]^-$ or $[Lac]^-$, whereas the CO_2/N_2 and CO_2/CH_4 permselectivities of those binary mixtures did not change much due to a significant decrease in their diffusivity selectivities. Even though linear trends

were not always observed relating gas permeability and diffusivity with viscosity, the overall results showed that mixing ILs having higher viscosities (carboxylated- or sulfate-based ILs) with those containing fluorinated- or cyano-functionalized anions decreases both the gas permeability and diffusivity through the SILMs. Also, the Camper Model[11] provides good descriptions CO_2/N_2 and CO_2/CH_4 solubility selectivity behavior for most of the pure ILs, but this model fails in describing the solubility selectivity of IL mixtures containing the $[Ac]^-$, $[Lac]^-$, $[N(CN)_2]^-$, or the $[C(CN)_3]^-$ anion, meaning that the IL molar volume as a single parameter cannot fully explain the solubility selectivity of those mixtures.

In sum, the results described in Chapter 3 clearly claim that IL mixtures are a powerful strategy for designing engineered membrane materials, since they offer a clear pathway to fine-tune their gas permeation properties as well as their CO_2 separation performances. On the other hand, these mixtures also offer valuable insights on the choice of functional groups that enable the design of efficient PILs for CO_2/N_2 and CO_2/CH_4 gas separation.

2. Designing PIL–IL composite membranes

Despite all the progress previously described in Chapter 1 concerning the use of polymeric ionic liquids (PILs) as a new generation of membrane materials for CO_2 separation, additional research is still required. The research work developed in the second part of this thesis not only contributed to better understand the relationship between PIL structure and gas transport properties but also to emphasize the potential of PILs as membrane materials for gas separation applications.

First, five membranes based on cationic PILs containing in their backbones the most important ionic liquid cations (imidazolium, pyridinium, pyrrolidinium, ammonium and cholinium) were prepared and gas permeation experiments were performed in order to fully explore the influence of polycation functionality on the

CO_2/CH_4 and CO_2/N_2 separation performances (Chapter 4). The obtained results contributed to understand the behavior and show the influence of polycation variation on the CO_2 separation performance of the prepared membranes. Albeit it is evident that the PIL polycation variation alone cannot promote the large improvement in gas permeability required for PIL-based membranes to be technologically competitive, the results of this study showed that the chemical structure of the polycation can play a role on the gas transport properties through PIL–IL composite membranes. Actually, membranes based on the tetra-alkyl ammonium-based PILs (pyrrolidinium, ammonium and cholinium) generally have lower gas permeabilities and diffusivities, whereas they present higher CO_2/CH_4 and CO_2/N_2 permselectivity values than membranes containing PIL imidazolium and pyridinium.

Bearing in mind the knowledge gained from the above mentioned study, and simultaneously considering that the synthetic route of pyrrolidinium-based PILs is less complicated than that used to prepare the commonly used imidazolium-based PILs and yields polymers with the same chemical properties such as for example, molecular weight, the pyrrolidinium polycation was selected to conduct the next studies. What is more, all the studies published up to the beginning of this PhD project involving PILs for CO_2 separation membranes were limited to the imidazolium polycation,[12-19] and the monomeric unit which contains the pyrrolidinium functionality has been proven to be more environmental-friendly than that of imidazolium.[20]

The feasibility of using pyrrolidinium-based PILs to prepare CO_2 separation membranes is addressed in Chapter 5. In this study, membranes within the whole range of compositions, from pure polymer to pure ionic liquid, encompassing PIL–IL composites, were evaluated. The incorporation of free IL into the polymer increased the gas permeabilities, overcoming the hindered diffusion of gas in the pure PIL-based membrane. Moreover, the analysis of the full material range not

only elucidated that the addition of free IL has the main role in the permselectivity of the prepared PIL–IL composites, but also allowed for the selection of the appropriate IL amount so that CO_2 separation membranes closer to the 2008 upper bound of the Robeson plots can be prepared. It is worthwhile mentioning that for the PIL–IL composite membranes with 20 and 40 wt% of free IL, the obtained CO_2/N_2 permselectivities were higher than that of both pure PIL and IL and, thus, surprising improvements of the CO_2/N_2 separation performance were achieved.

In order to increase the possibilities of designing CO_2 separation membranes based on pyrrolidinium-based PILs, a new family of pyrrolidinium random copolymers containing different anion mixtures was synthesized by simple and quantitative salt metathesis reactions, and subsequently PIL–IL composite membranes were prepared (Chapter 6). Although the initial idea behind this study was to select counter-anions with distinct chemical features, for synthetic reasons the anions used in this study were chosen based on their hydrophobic nature and the commercially availability of their respective salts. From the gas permeation results, it was possible to conclude that the permeability of all gases in the composite membranes is generally related to their gas diffusivities. In fact, depending on the structure of the second counter-anion, different permeation results were obtained which enables to infer that the polymer chains interact and pack differently and consequently rigid or further opened polymer networks can be obtained. The assessment of the mechanical properties endorsed that the composite membranes composed only of fluorinated based counter-anions are robust and flexible. Although the CO_2/CH_4 and CO_2/N_2 separation performances of the prepared membranes do not outperform the respective 2008 upper bound of the Robeson plot, emphasis should be given to the fact that this study opened new possibilities for designing promising PIL–IL composite membranes since their CO_2 separation performances as a function of permeability can be tuned by using

PILs with different counter-anions mixtures.

At this stage, it was clear that the development of pyrrolidinium-based PIL membranes that possesses higher CO_2 permeabilities would be crucial to make these membranes more attractive for industrial CO_2 separation applications. To achieve this goal and taking into account the valuable clues gathered from the previous studies with SILMs, the performance of pyrrolidinium-based PIL membranes may be improved by introducing other chemically different anions, for instance, by using anions with functional groups such as amines, nitriles, or carboxylates in order to create task-specific PIL–IL membranes.

In view of the above mentioned aspects, novel pyrrolidinium-based PIL–IL membranes containing different cyano-functionalized anions were proposed (Chapter 7). The PILs with high thermal stabilities were over again synthesized by straightforward anion exchange reactions and characterized. The gas permeation results showed that the presence of different cyano-functionalized anions has no effect on the gas solubilities of PIL–IL membranes, but depending on the number of cyano groups in the anion, different gas permeabilities and diffusivities can be obtained. It was also found that the incorporation of higher IL contents into the pyrrolidinium-based PIL with the tricyanomethane counter-anion not only dramatically increased the gas permeabilities and diffusivities through the composite membranes but also enhanced their CO_2/N_2 permselectivities. Importantly, the contribution of the solubility-controlled mechanism increases with the IL content and thus these composite membranes are, in fact, CO_2 solubility selective materials. It is worthy to note that this work highlighted for the first time a PIL–IL membrane that outperforms the Robeson 2008 upper bound for CO_2/N_2 separation. Nevertheless, further research should focus on long-term chemical and mechanical stability, as well as the effect of different experimental conditions (temperature, pressure and humidity) more close to the ones used in CO_2 separation processes in order to understand the full potential of the prepared

membranes.

In Chapter 8, the use of PILs as alternative polymer matrices to prepare membranes for ethylene/ethane separation was addressed. PIL–IL–Ag^+ membranes were successfully prepared by a solvent casting method. The addition of IL–Ag^+ decreased the gas permeabilities through the composite membranes as the silver concentration increased. On the other hand, the presence of the silver salt greatly boosted the solubility of ethylene, while the solubility of ethane remained almost constant, and consequently the ethylene/ethane permselectivity of the composites was essentially dominated by solubility selectivity. Regarding the separation performance of the prepared membranes, it was found that increasing the silver ion concentration leads to enhanced overall permselectivity surpassing the upper bound for polymeric membranes. In addition to the study of the effect of different experimental conditions, future research should be carried out in terms of long-term chemical and mechanical membrane stability and at developing an intrinsically stable carrier.

3. Outlook

Additional valuable clues regarding the role of diverse anions can be gathered from the results obtained throughout the studies presented in this thesis on the subject of SILMs. Indeed, ILs have been deeply researched and specifically designed to perform in a highly efficient manner for CO_2 separation applications, overcoming the drawbacks of some of the ILs initially proposed. The test and careful analysis of specific ILs in SILM configurations can provide important insights into the structure-property relationships, thus allowing a more confident design of PIL analogues.

During this thesis promising and innovative results were achieved for PIL-based membranes having functionalities never explored, whereas there still is a lack of diversity in what concerns the different chemical structures of cations and

anions. PILs having cationic, anionic and zwitterionic moieties in the polymer backbone have already been synthesized and used in other areas of knowledge,[21-23] but only the first class has been approached for the preparation of CO_2 separation membranes. It is indispensable to explore the performance of other PIL architectures in order to understand/identify the best performing polymers.

Another concern is the lack of data under real industrial conditions. The evaluation of the behavior of PIL-based membranes with temperature, at different humidity conditions and exposed to different chemical environments, is crucial for their application in CO_2 separation processes. Specific target operating conditions may be suggested: first, testing the efficiency of PIL-based membranes at high pressures, high temperatures and different compositions of binary gas mixtures, ranging from pure CO_2 to either pure CH_4 or N_2, depending on the separation envisaged; second, testing gases with different humidity contents and perform long-term experiments. Additionally, other important issue that should be considered on future research is the mechanical and chemical stability of the PIL-based membranes. Taking into account that membranes with CO_2 separation performances in the upper right quadrant of the Robeson Plots are very important for industrial applications, the development of PIL-based membranes targeting the critical combination of high CO_2 permeability/permselectivity and high chemical and mechanical stability is required to place these materials at the doorways of industrially relevant membrane-based gas separation processes.

The future use of membrane technology using the most promising materials developed in this thesis can also be envisaged. In particular, the development of methodologies to prepared thin films as well as the choice/fabrication of adequate supports would greatly boost the results obtained in this thesis. The implementation of the most efficient membranes in hollow fibers modules would also provide an interesting step towards the application of these membranes in real industrial conditions.

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"It is good to have an end to journey toward; but it is the journey that matters, in the end."

Ernest Hemingway